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AGRICULTURAL COLLEGE AND RESEARCH ... 27 30 AUG ...

A Journal of Theoretical and Practical Chemistry and Physics,

IN THEIR APPLICATION TO

ENGINEERING AND MANUFACTURES.

EDITED BY

J. G. F. DRUCE, M.Sc. (Lond.), R.Nat.Dr. (Prague).

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THE CHEMICAL NEWS.

VOLUME CXXIX.

Edited by J. G. F. DRUCE, M.Sc. (Lond.), R.Nat.Dr. (Prague), &c.

NO. 3351.—JULY 4, 1924.

THE CHEMICAL NEWS,

VOL. CXXIX. No. 3351.

THE STRUCTURE OF BISMUTH.

By HAWKSWORTH COLLINS, B.A. (CAMB.).

Although 208 is given by the International Committee as the atomic weight of bismuth, all the following varied *phenomena point to the number 209 as its* true atomic weight. The Odd and Even Rule (*The Chemical News*, 1913, CVIII., 235) also requires an odd number.

TABLE I.

Facts from the Periodic Table.

Monads		Pentads.		Remark.				
K	39	V	51	51	=	39	+	12
Cu	63	As	75	75	=	63	+	12
Ag	107	Sb	119	119	=	107	+	12
Au	197	Bi	209	209	=	197	+	12

Table I. shows that a difference of 12 in the atomic weight in each case corresponds with a difference of 4 valences. (Carbon of atomic weight 12 has 4 valences).

TABLE II.

Pairs of elements, whose atomic weights differ by 90, which are in the same column of the Periodic Table, also which are especially associated in mineralogy, and which frequently have the same volume.

						Relative Volume common to both.
Si	28	Sn	118	=	90+ 28	
Cb	94	W	184	=	90+ 94	
Ru	101	Os	191	=	90+101	9.05
Rh	102	Ir	192	=	90+102	9.05
Pd	104	Pt	194	=	90+104	9.05
Ag	107	Au	197	=	90+107	10.25 & 13.29
Sb	119	Bi	209	=	90+119	21.29
Ba	136	Ra	226	=	90+136	

The experimental atomic weight of Pd is nearer to 106 than 104, probably because it is impossible to separate completely Pd and Pt. The fact that the two of a pair have atomic weights differing by 90 and at the same time frequently have the same volume, shows that a constituent part of the heavier atom of a pair has a mass of 90 which is frequently completely absorbed by the remainder of the atom.

TABLE III.

Experimental data in support of the Relative Volumes in Table II.

	Relative Volume.	Theor. S.G.	Obs. S.G.	
(107)	AgI 10.25 + 32.77	5.44	5.470	0° Deville, 5.35 Schiff
(108)	Au 10.25	19.22	19.207	Elliot, 19.258 Brisson
(109)	$AgNO_3$ 13.29 + 3.8 + 3(7.53)	4.26	4.253	to 4.271 Schroder
(110)	$Ag_{10}Au_4S_{11}$ 10(10.25) + 4(13.29) + 11(10.51)	8.15	8.159	Muir
(111)	Ru 9.05	11.27	11.0	to 11.4 Deville
(112)	Os 9.05	21.1	21.4	Deville
(113)	Rh 9.05	11.27	11.2	Cloud, 12.1 Deville
(114)	Ir 9.05	21.21	21.15	Deville, 21.78 Boye
(115)	Pd 9.05	11.49	11.4	Deville, 11.628 Benneke
(116)	Pt 9.05	21.45	21.45	Berzelius
(117)	Sb_2S_3 2(21.29 + 10.51) + 15.53	4.22	4.223	23° Cooke
(118)	Bi 21.29	9.82	9.82	Roberts & Wrightson

Table I. suggests that Bi may have been formed from Au and C; and Table II. that it may have been formed from Zr and Sb, whilst the mineralogical fact that it is intimately mixed in the native state with $CoAs_2$ (Mol. Wt. 209) suggests that it may have been formed by the atomisation of this molecule. By the Inter-relationship of the Elements (*The Chemical News*, 1920, CXX., 169) these all ultimately represent the same thing, and are all included in the formula:

$$Bi = \begin{matrix} S & As \\ & & C \\ Al & Cu \end{matrix}$$

where AlS = Co, AlCu = Zr, AsS = Ag, CuC = As, AgC = Sb, ZrAg = Au.

It will now be proved by means of the laws of heat of formation and of relative volume that this structure is correct.

TABLE IV.

The Relative Volumes of Bismuth.

Bi	=	Zr	+	Sb
21.29	=	0	+	21.29
24.29	=	3	+	21.29

The former may be given as

Bi	=	Zr	+	Ag	+	C
21.29	=	0	+	13.29	+	8

or as

Bi	=	Au	+	C
21.29	=	13.29	+	8

and the latter as

Bi	=	Zr	+	Ag	+	C
24.29	=	3	+	13.29	+	8

TABLE V.

Experimental Data illustrating the Volumes of Table IV.

		Relative Volume.	Theor. S.G.	Obs. S.G.	
(119)	Bi_2S_3	2(21.29) + 3(10.51)	6.94	7.00	Karsten
(120)	Bi_2S_3	2(21.29) + 2(10.51) + 15.53	6.5	6.5	Dana
(121)	$PbS.Bi_2S_3$	20.45 + 15.53 + 2(21.29) + 3(10.51)	6.83	6.88	Sjogren
(122)	$2PbS.Bi_2S_3$	2(20.45 + 15.53) + 2(21.29) + 3(10.51)	6.77	6.75	Falun
(123)	$PbS.Sb_2S_3$	20.45 + 15.53 + 2(21.29) + 3(10.51)	5.2	5.21	18° Hillebrand
(124)	BiI_3	21.29 + 3(27.75)	5.644	5.64	to 5.65, 20° Gott
(125)	Bi_3As_4	3(21.29) + 4(11.38)	8.47	8.45	Descamps
(126)	$SbAs_3$	21.29 + 3(11.38)	6.206	6.203	Rammelsberg
(127)	$BiPO_4$	21.29 + 14.56 + 4.45 + 3(2.51)	6.356	6.323	Chem. Kal.
(128)	$SrHPO_4$	19.56 + 5.76 + 14.56 + 4.45 + 3(2.51)	3.548	3.544	15° Nostrand
(129)	Bi_2O_3	2(21.29) + 4.45 + 2(2.51)	8.95	8.8	to 9.0 Nostrand
(130)	Bi_2O_3	2(24.29) + 3(2.51)	8.3	8.5	Dumas, 8.21 Herapath
(131)	$Cu_2Bi_2S_4$	2(9.54 + 21.29) + 4(10.51)	6.48	6.3	to 6.5 Dana
(132)	Bi_2S_2	21.29 + 24.29 + 2(10.51)	7.24	7.29	Werther
(133)	$BiCl_3$	24.29 + 3(15.085)	4.54	4.56	11° Nostrand
(134)	$Bi(NO_3)_3 + 5H_2O$	24.29 + 3(3.8) + 9(7.53) + 5(14.03)	2.79	2.78	Nostrand
(135)	$NaNO_3$	11.85 + 3.8 + 3(7.53)	2.223	2.2256	Karsten
(136)	AgI	13.29 + 27.75	5.702	5.707	Damour
(137)	$MgCO_3$	7.51 + 8 + 7.53 + 2(2.51)	3.0	3.007	Jenzsch
(138)	Na_2CO_3	2(11.85) + 8 + 7.53 + 2(2.51)	2.40	2.407	Favre

(3 is sometimes the volume of Zr when forming part of other elements; *e.g.*, Pt = ZrPd = 9.05 and 12.05).

(139)	K_2PtCl_6	2(18.05) + 9.05 + 6(15.085)	3.575	3.586	15° Bodeker
(140)	K_2PtCl_6	2(18.05) + 12.05 + 6(15.085)	3.498	3.499	24°/4 Nostrand

TABLE VI.

Heat of Formation of Bismuth.

	H.F.	Original Volume		Rel. Vol. in combination at 15° C.		Change of Volume.
(a)	-75200 = 120 × (-3) × 209	21.29	=	24.29	-	3
(b)	0 = 120 × 0 × 209	21.29	=	21.29	+	0

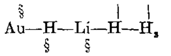
The H.F. of Bi_2O_3 is -2(75200)+3(96155) = 138065 139200 (obs.), which corresponds exactly with No. (130), Table V.

The H.F. of $BiCl_3$ is -75200+3(56786)= 95158 90800 (obs.), and 98460 aq., which corresponds with No. (133), Table V.

The H.F. of BiO_3H_3 is -75200+3(96155) -3(15300)=167165 171700 (obs.). There is no S.G. of this substance available.

The above are the only compounds of bismuth of which values for H.F. are given in Nostrand's Annual. They are all examples of (a), Table VI., so that no examples can be given of (b).

Preceding facts demonstrate that the constitution and structure of an atom of bismuth is



'our of its valences emanating from a mass)f 12, whilst the fifth comes from a mass)f 197. The lines between the five por-:ions represent atomic internal bonds, the ,wo thick lines are electro-positive valences md the curly lines electro-negative forces.

The volume occupied by the mass of 12 at 15° C. is 8.0, which is the same as that occupied by an atom of carbon in carboxyl, whilst the volume 13.29 of the mass of 197 is the same as one of the two volumes which is common to both Au and Ag.

21.29 is the usual volume of bismuth; but Thomsen found the H.F. of $BiCl_3$ directly, and this substance happens to contain the larger, 24.29, of the two volumes of Bi. He then calculated the H.F. of other compounds from it.

SUMMARY.

The constitution and structure of an atom of bismuth which had previously been obtained (*The Chemical News*, 1920, CXXI., 220) by means of reasoning upon Atomic Weight, Valency, Periodic Table, and the Odd and Even Rule, is here proved to be correct quite independently by means of the Laws of Relative Volume and Heat of Formation.

In addition to the support given to these two laws, the demonstration of Specific Gravity as an exact instrument of research is considerably extended.

CHLORINE GAS AND POWER STATION EFFICIENCY.

THE "CHLORONOME" PROCESS FOR THE TREATMENT OF COOLING WATER FOR STEAM TURBINE CONDENSERS.

A highly ingenious and scientific prin-iple for the improvement of steam power lant efficiency is that underlying the Chloronome" apparatus. This is an rrangement for adding continuously and utomatically a measured small trace of hlorine gas to cooling water for steam en-ine and turbine condensers, so as to prevent the growth of microscopic organisms on the inside of the condenser tubes, forming a slimy deposit which rapidly reduces the heat conductivity, and thus lowers the vacuum. As is well known, the efficiency of a steam turbine depends very largely on the maintenance of the highest vacuum, and a fall of, say 1 inch, from 28¾ inch, approximately the correct figure, increases the steam consumption of a turbine 5-6 per cent. Previously the only method of attempting to remedy the trouble has been by hand cleaning, which is laborious, costly, and, above all, inefficient, whilst

involving in many cases the use of practically an additional condenser.

By means of the "Chloronome," which is the invention of Messrs. The Paterson Engineering Co., Ltd., of London, an amount of chlorine is added to the water, which generally averages not more than one part per three million parts of water. This excessively small amount is sufficient to prevent the growth of all organic matter, effecting what may be termed a semi-sterilisation, and without any trouble keeps the tubes permanently in a clean condition, whilst of course there is no deleterious action whatever on any part of the plants.

The apparatus for large volumes of water, 2,000,000-75,000,000 gallons per 24 hours is of the "Manometer" type, and consists essentially of a control board connected to cylinders of chlorine, now easily obtainable at about 4d. per lb. because of the great increase in the use of processes involving the electrolytic treatment of brine. On the control board is fitted a filter for the chlorine, and two reducing valves, one after the other, the first of which reduces the pressure more or less to 30 lbs. per square inch, whilst the second controls and reduces it very accurately to 10 lbs., and there is also a control valve and meter, so that any amount may be passed in, as seen by gauges. The chlorine gas bubbles through a patent seal of concentrated sulphuric acid, which prevents any moisture passing back into the apparatus from the water, so that the chlorine is maintained in a dry state up to the seal, and subsequently passes to a small vertical absorbing tower, constructed of glazed earthenware and filled with pumice stone, down which a tiny trickle of water is allowed to pass. The chlorine enters the bottom of the tower and is completely absorbed, the water running out at the bottom containing the whole of the gas in the form of a dilute solution, which passes into the main supply of the cooling water.

MOTOR FUEL.

A recent U.S. patent has been taken out for a liquid fuel, consisting of a eutectic mixture of cyclohexane and benzene.

A FURTHER STUDY OF THE NEUTRAL AMMONIUM SALTS OF SOME ORGANIC ACIDS AND THEIR SUBSTITUTED DERIVATIVES.*

By LeRoy McMaster and Paul K. Pratte.

[*Contribution from the Chemical Laboratory of Washington University.*]

This work is a continuation of the investigation which has been in progress in this Laboratory on the preparation and properties of the neutral ammonium salts of organic acids and their substituted derivatives. The salts described in this paper were, with slight modifications in several instances, prepared by the same general method as was used in the previous investigations, that is, by passing dry ammonia into solutions of the acids in those anhydrous organic solvents in which their salts were found to be insoluble. When it was found that an acid and its ammonium salt were both soluble in a certain solvent, the solution of the ammonium salt was poured into an excess of another solvent in which the salt was insoluble. In several cases it was necessary to evaporate the solutions nearly to dryness before the salts crystallised. In the case of acetyl *m*-aminobenzoic acid, it is insoluble in all the common organic solvents that do not react with ammonia, and its solubility in water is very slight. It is soluble in concd. ammonium hydroxide. The neutral ammonium salt was thus prepared by dissolving the acid in concd. ammonium hydroxide, evaporating the solution to dryness, and then passing ammonia into an alcoholic suspension of the residue.

Of the neutral salts described in this paper, none has been previously prepared except those of phenoxyacetic acid[1] and 2,5-dichlorobenzene sulphonic acid.[2] They were prepared by neutralising an aqueous solution of the acid with ammonium hydroxide. The ammonium 1,2,4-dinitrobenzoate was described in a previous paper,[3] but we have determined its solubilities and recorded them in this work.

*[*Reprinted from the "Journal of the American Chemical Society," Vol. XLV., No. 12, December, 1923.*]

[1] Fritzsche, *J. prakt. Chem.*, 1879, (2), XX., 269.

[2] Lesimple, *Z. Chem.*, 1868, IV., 226.

[3] McMaster and Wright, *Jour. Amer. Chem. Soc.*, 1918, XL., 683.

Solubility determinations were made of only the stable salts by the analytical method. By this method the salt, in excess, was stirred with the solvent at a definite temperature until equilibrium was reached. The excess of salt was allowed to settle and the clear liquid decanted off into a weighed evaporating dish and immediately weighed. When the solvent had completely evaporated the evaporating dish was again weighed. From the differences in weight the amount of salt soluble in the solvent at the given temperature could be calculated. All the solubility determinations were carried out at 20°, which temperature was maintained in an automatic water thermostat. A large test-tube was used to hold the solubility mixture and was fitted at the top with a mercury seal to prevent the absorption of water vapour from the air by the solvent. This seal was constructed by sinking a piece of glass tubing (a 25 mm. section of a large test-tube) into a cork containing a glass bearing for the stirrer. The space between the tube and the bearing was then filled with mercury. A second tube, smaller than the first, was then tightly fastened to the stirring rod by means of a cork, so that when the stirrer extended to the bottom of the test-tube, the second tube fitted within the bearing and the large tube at the same time dipped below the surface of the mercury. In this manner the contents of the test-tube could be sealed against contact with air, and at the same time the solution thoroughly stirred at about 200 r.p.m. It was found by experiment that 20 minutes was suffi-

TABLE I.

Properties and Analyses of Neutral Ammonium Salts.

Acid	Stability in dry air (+ = stable;	Stability in moist air − = unstable)	Nitrogen Calc. %	Nitrogen Found %
Iodo-acetic	−	−	6.89	6.90
Phenoxyacetic	+	+	8.28	8.29
p-Nitrophenylacetic	+	+	14.14	14.08
β-Bromopropionic	−	−*	8.23	7.98
α-Bromo-*n*-butyric	−	−*	7.61	7.48
o-Iodobenzoic	+	−	5.28	5.30
p-Iodobenzoic	−	−	5.28	5.24
o-Methoxybenzoic	+	+	8.28	9.32
Acetyl *m*-aminobenzoic	−	−	14.28	14.19
Acetyl *p*-aminobenzoic	−	−	14.28	14.30
5-Nitrosalicylic	+	+	14.00	14.00
α-Naphthalenesulphonic	+	−	6.22	6.28
β-Naphthalenesulphonic	+	+	6.22	6.26
2,5-Dichloro-benzenesulphonic	+	+	5.74	5.70
4-Nitrochloro-benzene-2-sulphonic	+	+	11.00	11.00

* Deliquescent.

TABLE II.

Solubilities of Neutral Ammonium Salts.

Acid	Water	Solvent CH_3OH	C_2H_5OH
Phenoxyacetic	13.03	3.97	0.44
p-Nitrophenylacetic	7.41	15.14	1.82
o-Iodobenzoic	67.11	184.10	63.37
o-Methoxybenzoic	38.25	17.85	4.82
1,2,4-Dinitrobenzoic	62.70	21.39	3.85
5-Nitrosalicylic	4.43	4.41	1.96
α-Naphthalenesulphonic	45.91	34.45	9.22
β-Naphthalenesulphonic	11.71	8.33	2.53
2,5-Dichloro-benzenesulphonic	11.30	20.15	2.59
4-Nitrochloro-benzene-2-sulphonic	4.72	2.76	0.96

cient to bring the solution to equilibrium with the salt. The solubilities so found are expressed in grams of salt per hundred grams of solvent.

In the preceding tables are recorded several of the properties, the results of analysis and the solubilities of the neutral ammonium salts of the acids listed.

SUMMARY.

Fifteen neutral ammonium salts of organic acids have been prepared by the action of dry ammonia on solutions of the respective acids.

The stabilities in dry and moist air and some of the solubilities have been determined.

St. Louis, Missouri.

GENERAL NOTES.

THE DEPOSITS OF MOLYBDENUM ORE IN CANADA.

Molybdenum is never found in the metallic state in nature, but occurs as molybdenite, the sulphide of molybdenum, or wulfenite, in which the metal is combined with lead and oxygen. Wulfenite is not known to occur in Canada.

Molybdenite is a silver white, soft, pliable mineral, that leaves a blue-grey mark when rubbed on paper, and has the appearance and feel of freshly cut lead foil. It has many uses, such as in electrical appliances; as a substitute for platinum, which it closely resembles, both in appearance and physical properties, but by far the most important use, as an alloy in steels.

War demands greatly stimulated its production, particularly as the supplies of tungsten, which was previously used (as it imparts somewhat similar properties to steels) were mainly cornered by Germany. Early in the war, the Imperial Government issued an embargo within its colonies, commandeering all the available supplies of certain metals, including molybdenum, and controlled the prices.

The Mines Branch of the Department of Mines, Ottawa, acted as Canadian agents in the buying of ores and concentrates, and treated many thousands of tons of raw molybdenite ore from all over the Dominion. Before the war production in Canada was practically nil, and there were very few known deposits of the mineral, but the new demand led to so much interest and activity that there are now about 350 recorded occurrences. The Imperial Government apparently did not realise the hidden resources of this mineral within the Dominion, and early in 1919 cabled that British war requirements in molybdenum were filled. Prices suddenly fell, and operations ceased at a time when most of these occurrences were only imperfectly known, and when extensive production from the better known deposits was getting well under way. In the peak year of 1918 Canada became the second largest world's producer of molybdenum. Most of the output came from a deposit at Quyon, Quebec, thirty miles west of Ottawa, which for some time was the world's leading individual producer. During the war period molybdenite was mined from 110 different properties, from 30 of which over 5 tons of ore were shipped or treated.

Molybdenite occurs in practically every province in Canada, but the greatest number of known deposits lie within a wide 150 mile belt to the west and south of Ottawa. In British Columbia there were no molybdenite concentrators, so that all the ore was shipped directly to the Mines Branch, Ottawa, where the one to three per cent. ore was concentrated to eighty-five per cent. or over of molybdenite. The long haul naturally retarded development and production, and furthermore, when the producers were ready to instal their own plants, the market collapsed. Several of these western properties might become producers should a demand arise, and many of the Ontario and Quebec shippers who closed down in 1919 still have considerable supplies of unmined ore. Although there has been no production from Canada during the last four years, at least four companies, who were too late to ship during the war have continued the development of their properties, and contemplate producing in the near future.

During the war two companies in Canada treated the molybdenite concentrates and made an alloy with iron, called ferromolybdenum, in which form it was shipped to England. They also made molybdenum salts, used in the analysis of steels and other metals.

Since the war, although very little molybdenum ore has been mined through-

out the world, many experiments in the making and testing of commercial molybdenum steels have been undertaken by independent investigators. In consequence of this, the beneficiary results claimed in what are known as low molybdenum alloy steels (one-fourth of one per cent. of molybdenum or under) have been proved. These steels are now used for structural and engineering purposes where great stresses and strains are involved. The beneficent qualities of molybdenum may be summarised in saying that when it is added in small quantities to an alloy steel it acts as a stabiliser or corrective against the undesirable qualities of the other elements present in that alloy. A recent investigator states that it is the most active and potent element in steel. The sudden cessation of demand for war purposes; the very gradual increase in commercial uses, and the enormous stocks on hand, are all factors that have caused the world's production of molbdenum to be practically negligible during the last three years. Stocks are now greatly diminished, and commercial uses are steadily increasing, so that it is confidently expected that mining will soon be resumed, and in consequence of this, the Mines Branch of the Department of Mines, Ottawa, has made a special investigation of the molybdenum ore resources of Canada, and has found them to be large enough to ensure the production of considerable quantities when the demand arises. The detailed result of the investigations will be published within the year.

CANADIAN TALC RESOURCES.

Canada stands sixth on the list of the world's talc-producing countries, and in 1922 produced over 12,000 tons, most of which was ground talc. There are three producing regions, in Quebec, Ontario, and British Columbia respectively, that in Ontario being the most important.

Talc of fair quality occurs in the Eastern townships of Quebec, but has never been actively worked. The deposits consist of bands of altered schist that can be traced for considerable distances. These bands are made up of thin, fissile layers of talc, which, when ground, yields a grey or cream powder, possessing high slip. The deposits are large enough to yield a considerable tonnage o grey talc, well suited to the requirements of the paper, rubber and paint trades, and fully the equal of the best talc mined in the adjacent State of Vermont, U.S.A. Talc rom ermont is imported into Canada in considerable quantities, and could well be replaced by the domestic product. Latterly, small amounts of bloc talc from the Quebec field have been used as lining material for the smelting furnaces of sulphate pulp mills in the province; but the stone is considerably checked and flawed, and does not cut as strong a brick as the regular soapstone ordinarily used. Large deposits of the latter grade of stone have recently been discovered in Western Ontario, and it is expected that their exploitation will be taken in hand at an early date.

The Ontario talc industry centres around the town of Madoc, midway between Ottawa and Toronto, where three mines, each equipped with a mill, have been opened up on lenticular bodies of foliated, white tal cenclosed in white, crystalline dolomite. The mills make a very high grade of white talc, which finds its principal market in the talcum powder, textile, paper, soap and rubber trades. A great deal of the talc from this district is exported to the United States, and a growing interest is being shown in it by the trade in Great Britain.

In British Columbia, a belt of talc-bearing rocks extend for many miles in the lower Fraser River country and along the Pacific Great Eastern Railway, and a small amount of grey talc has been taken from this region, principally for use in roofing materials.

Similar talc is found also on Vancouver Island, near Victoria, and is worked on a small scale. A deposit of fine, cream-coloured steatite, or massive talc, was discovered some years ago just west of the British Columbia-Alberta boundary, near Banff, but the true character of the material has not been determined. It may prove suitable for gas burner (lava) purposes, provided it is not subject to the checking which so often spoils steatite for this use.

DEATH OF SIR JAMES J. DOBBIE.

The death has occurred at his residence, The Cottage, Fairlie, of Sir James Johnston Dobbie, LL.D., F.R.S., who, until a few years ago, was Government Chemist

at the Government Laboratories, London, and has since rendered useful service on the Royal Commission on Awards to Inventors.

Sir James Dobbie was born in Glasgow in 1852, and was educated at the High School and Glasgow University, where he graduated in arts, with first-class honours in natural science, and obtained the George A. Clark Scholarship. He studied later at Leipzig and Edinburgh, taking his D.Sc. at the latter University. After a period as Lecturer in Mineralogy at Glasgow University, he was appointed in 1881 assistant to the Professor of Chemistry, which he held until his presentation to the Chair of Chemistry in the University College of North Wales at Bangor. His services as a scientific chemist were not confined to the problems of pure science dealt with in his published papers. Much of his attention was devoted to the introduction of new methods of agricultural education, and his services in this direction were cordially acknowledged by the Board of Agriculture. In 1903 he accepted the post of director to the Royal Scottish Museum, Edinburgh, which he held for six years, relinquishing it on his appointment as Government Chemist at the Government Laboratories, where he did valuable work throughout the war and until his retirement in 1920. Since then he had given much time to the affairs of the Royal Commission on Awards to Inventors, of which he was a member. He was also on the University Grants Committee. In 1915 his services to science, both as investigator and administrator, were recognised by the King, who conferred a knighthood on him. In 1904 he had been elected a Fellow of the Royal Society, in recognition of the value of his numerous publications on the chemical constitution of alkaloids and the relation between the chemical constitution and the absorption spectra of chemical compounds. Four years later Glasgow University conferred on him the honorary degree of LL.D. He was a past president of the Institute of Chemistry, and of the Chemical Society. Sir James Dobbie is survived by his wife and one son and two daughters, one of his daughters being the wife of Professor Haworth, Armstrong College, Newcastle-on-Tyne.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE ROYAL SOCIETY.

JUNE 26.

Papers read:—

J. W. NICHOLSON, F.R.S. *The Electrification of Two Parallel Circular Discs.*

J. F. FULTON. *The Influence of Initial Tension upon the Magnitude and Duration of the Mechanical Response in Skeletal Muscle.* Communicated by Sir Charles Sherrington, P.R.S.

J. R. H. COUTTS, E. M. CROWTHER, B. A. KEEN, and S. ODEN. *An Automatic and Continuous Recording Balance. (The Odén-Keen Balance).* Communicated by Sir John Russell, F.R.S.

R. W. LUNT, PH.D. *Chemical Studies in Gaseous Ionisation: Part I. and Part II.* Communicated by Prof. F. G. Donnan, F.R.S.

This communication described the method used for producing ionisation, namely, the corona due to alternating electric fields of frequency 1.5×10^7, and the measurement of the ionisation so produced in hydrogen.

The conditions of generation of single phase alternating current of the above frequency are described in some detail, together with the technique that has been developed for the measurement of current and voltage.

A new analysis of the Siemen's ozoniser is advanced which affords a ready determination of the voltage gradient in the gas, and of the current carried by the ions in the gas.

The mean intensity of ionisation has been calculated from an equation relating the conduction current in the gas to the known motions of ions and electrons in hydrogen.

The interaction between hydrogen and carbon dioxide due to the ionisation produced by alternating electric fields of frequency 1.5×10^7 has been examined under a variety of conditions.

An equimolecular mixture interacts giving a water gas equilibrium, which is also attained by exposing mixtures of carbon

monoxide and water vapour to the discharge. In no case has it been possible to detect the formation of formic acid or formaldehyde.

The equation used in Part I. of this series for the determination of the mean intensity of ionisation in hydrogen has been extended to the determination of this quantity in the above-mentioned water-gas equilibria.

D. W. DYE. *A Self-Contained Standard Harmonic Wavemeter.* Communicated by Sir Joseph Petavel, F.R.S.

Papers read in title only:—

W. L. BRAGG, F.R.S. *The Influence of Atomic Arrangement on Refractive Index.*

In the calculations of refractive index made in this paper, it is assumed that the atoms, which are polarised by the electric force associated with the light wave, are spherically symmetrical ions. It is further supposed that the elastic yield of the ion to the polarising force is defined by a coefficient λ, which is a constant for the ion concerned, and that the polarising force may be taken to be that at the atomic centre.

The author has shown in a previous paper that it is possible with these assumptions to explain quantitatively the birefringence of calcite and aragonite, using the X-ray determinations of crystal structures. The birefringence of aluminium oxide is explained in a similar way in this paper, the process of calculation leading to more accurate results than in the case of calcite. The refractivities of the alkaline halides determined recently by Spangenberg are discussed with a view to testing the assumptions on which the calculations have been based. An attempt is made to attack the reverse problem of using the refractivity data to give information about crystal or molecular structure. It is shown that a comparison of refractivity in carbonates and nitrates indicates a contraction of the NO_3 group as compared with the CO_3 group, and a value for the distance between nitrogen and oxygen atomic centres is obtained. Finally, the possibility of extending similar reasoning to the case of gaseous molecules is discussed.

PROF. A. V. HILL, F.R.S., and H. S. GASSER. *The Dynamics of Muscular Contraction.*

G. S. CURREY. *The Colouring Matter of the Blue Pansy.* Communicated by Sir Frederick Keeble, F.R.S.

1. The Anthocyanin pigment of the blue pansy "Emperor William" consists of Violanin, and the blue colour of the petals is due to the fact that the pigment is present in the form of its potassium salt; it occurs to the extent of ca. 6.3 per cent. by weight of the dried petals (= 1.14 per cent. of the fresh petals).

2. The yellow sap-pigment occurring in the same flowers consists of the flavonol, rutin (viola-rutin). As crude glucoside, it is present to the extent of ca. 9.68 per cent. by weight of the dried petals (= 1.75 per cent. of the fresh petals), the actual amount of pure rutin being 50.4 per cent. by weight of the crude substance, *i.e.*, the dried petals contain approximately 4.9 per cent. of pure rutin (= 0.88 per cent. of the fresh petals).

R. SNOW. *Conduction of Excitation in Stem and Leaf of Mimosa pudica.* Communicated by Dr. A. Church, F.R.S.

R. AZUMA. *Thermodynamic Phenomena exhibited in a Shortening or Lengthening Muscle.* Communicated by Prof. A. V. Hill, F.R.S.

H. TAYLOR. *The Ionic Nature of Hæmoglobin.* Communicated by Prof. A. V. Hill, F.R.S.

A method is given of ascertaining the ionic contents of the blood corpuscle and the magnitude and sign of the charge on the hæmogoblin molecules existing there. This is done by laking the corpuscles by freezing and thawing and suspending in them a collodion membrane which contains a dilute salt solution and which is impermeable to hæmogoblin. A Donnan equilibrium is thus obtained after about three hours. The membrane potential difference is then measured and this gives the factor relating the ionic concentrations of the laked corpuscles and those of the crystalloid solution inside the collodion membrane. From this potential difference and an analysis of the crystalloid dialysate the concentrations of the hydrogen and chlorine ions in the laked corpuscles has been determined.

The sign of the potential difference shows whether the hæmogoblin is behaving as a cation, an anion, or as an undisso-

ciated colloid. The potential differences found indicate that the hæmogoblin is behaving as an anion over the range of physiological importance. The normality of the hæmogoblin ions present has been calculated from the potential difference and the concentration of anions in the dialysate. *The quantities obtained indicate the maximum amounts of CO_2 the blood can further take up as bicarbonate.*

J. Stephenson, D.Sc. *On the Blood-Glands of Earth-worms of the genus Pheretima.* Communicated by Prof. J. H. Ashworth, F.R.S.

H. Muir Evans. *Supplementary Note on the Poison Gland of Trygon.* Communicated by Dr. H. H. Dale, F.R.S.

E. M. Crowther and A. N. Puri. *The Indirect Measurement of the Aqueous Vapour Pressure of Capillary Systems by the Freezing Point Depression of Benzene.*

The validity of an indirect method for the measurement of aqueous vapour pressures has been tested. The freezing-point of benzene is depressed by an amount which is strictly proportional to the aqueous vapour pressure of an insoluble material with which it is in equilibrium, provided that surface energy is not one of the factors determining the vapour pressure of this material. The method is both rapid and accurate when applied to substances such as sulphuric acid-water mixtures and certain salt hydrates. With capillary systems such as soil, the equilibrium is reached more slowly and the apparent vapour pressures show a systematic deviation, which is the same for soils of widely different types. It is shown that, by assuming that a fraction of the water in such cases is held in micropores and making allowance for the effects of the changes in surface energy on the introduction of an additional liquid phase, it is possible to account for this deviation. The agreement between the observed values and those calculated on this assumption is taken to afford evidence of the manner in which water is held in moist capillary systems.

B. Cavanagh. *Activity-Measurement by the Partition Method. I.* Communicated by Prof. J. W. Nicholson, F.R.S.

A new way of applying the partition-ratio is suggested, as an indirect means of precise activity-measurement, possessing unique possibilities in certain cases. In pursuance of this idea an experimental *method has been devised for the precise measurement of a partition-ratio at extremely low concentrations, and preliminary measurements, in the case of lithium chloride between amyl alcohol and water, are recorded, in which the normality, N/8000 (in the alcoholic phase),* has been reached, with satisfactory concordance in triplicate measurements. The method consists essentially in the piecemeal preparation of a large amount of the phase to be analysed, and the concentration (for chemical estimation) of the solute therefrom, by a process of piecemeal extraction. As a method of precision, it rests upon the possibility of exactly calculating, and applying by successive approximations, a correction for the amount of the solute evading extraction.

Approximate values have been obtained, for the first time, for the activity coefficient of lithium chloride in amyl alcohol, at normalities ranging from 0.2 to 0.0001.

J. E. Jones, D.Sc. *On the Determination of Molecular Fields. Part I. and Part II. Communicated* by Prof. S. Chapman, F.R.S.

By applying the methods of the kinetic theory to a new molecular model, a new theoretical formula for the coefficient of viscosity of a gas has been obtained. This is of a more general character than previous formulæ, and gives a closer representation of the observed variation of viscosity with temperature. In the case of argon *the difference between theoretical* and experimental values is nowhere greater than 0.6 per cent. over the whole range of the observations (-180° to 180° C.), whereas other formulæ have resulted in a discrepancy as much as 8 per cent. at low temperatures. The molecular field of this gas is considered in some detail by means of the formulæ given in the paper.

The equation of state of a gas has been *calculated for a molecular model* consisting of repulsive and attractive fields, each according to an inverse power law. The formula for the *second viriel coefficient* thus obtained contains existing formulæ (for a monatomic gas) as special cases. A method is developed of obtaining the force

constants of a gas, both attractive and repulsive, from a comparison of the theoretical formula with observational material on the equation of state. In the case of Argon, considered in detail, it is shown that more than one molecular model will explain the facts.

C. J. Smith. *An Experimental Study of the Viscous Properties of Water Vapour.* Communicated by Prof. H. C. Callendar, F.R.S.

The viscosity of superheated water vapour over the range of temperature 100°-260° C. has been determined. The method used involves the transpiration of the superheated vapour through a capillary tube, special devices being adopted to determine the pressure at the ends of the capillary tube and the mass of the vapour transpired. The results show, within the limits of experimental error, that the variation of the viscosity with temperature can be represented by Sutherland's formula.

The dimensions of the water molecule, the evaluation of which is rendered possible by the results, are in accordance with previous investigations for other gaseous hydrides.

E. M. Crowther and J. R. H. Coutts. *Discontinuity in the Dehydration of Certain Salt Hydrates.* Communicated by Sir John Russell, F.R.S.

The changes in weight on rapidly drying certain salt hydrates have been recorded continuously by means of the Odén-Keen automatic recording balance. With thin layers of small crystals of copper sulphate pentahydrate and barium chloride dihydrate, the rate of evaporation shows a very marked minimum value at points corresponding to the composition of definite lower hydrates. A tentative explanation of this phenomenon and of the course of the evaporation under certain other conditions is advanced on the basis of Langmuir's theory that heterogeneous reactions proceed only at the actual phase boundary.

No evidence of discontinuities was found in the rehydration of anhydrous copper sulphate.

W. R. Dean. *The Elastic Stability of an Annular Plate.* Communicated by Prof. G. I. Taylor, F.R.S.

R. C. Johnson and W. H. B. Cameron. *The Effect of Argon on certain Spectra.* Communicated by Prof. T. R. Merton, F.R.S.

The present paper describes work which is a natural sequence to that published by Merton in connection with modifications induced in spectra by the presence of helium. Investigations have been made of the effect of Argon on spectra associated with carbon, oxygen and sulphur, and it is clear that while in certain respects the action of argon and helium is similar there are also profound differences. Notable among the latter is the fact that it has not been found possible to reproduce the "Comet-Tail" bands in high pressure argon. The "Triplet System" of carbon is isolated, however, by both the inert gases. An effect of a similar type due to argon has been observed in connection with sulphur dioxide. A band spectrum of the latter (obtained otherwise only with difficulty) was brougbt up strongly on the presence of high pressure argon; this spectrum was measured and series formulæ calculated. Other changes induced by argon in the fine structure of certain bands are described, and a brief discussion of the nature of the action of the inert gases is presented.

G. R. Goldsbrough, D.Sc. *On the possible Ellipticity of Saturn's Ring.* Communicated by Prof. T. H. Havelock, F.R.S.

Maxwell showed that a single circular ring of particles surrounding the planet Saturn would be in relative equilibrium, provided the mass of each particle was sufficiently small compared with the mass of Saturn. In the present paper this result is extended to the case of an elliptical ring. It is shown by properly placing the particles on the ellipse, by allowing the ellipse to rotate slowly in its plane, and the particles to vibrate about their mean positions, that the elliptical ring is a possible dynamical form.

An investigation into the stability of such an arrangement shows that for sufficiently small values of the mass of the particles, and for values of the eccentricity not too great, the elliptical ring will be "ordinarily" stable.

E. C. Titchmarsh. *The Double Fourier Series of a Discontinuous Function.* Communicated by Prof. G. H. Hardy, F.R.S.

ROYAL SOCIETY OF ARTS.

A meeting of the Indian Section was held on June 30. A paper entitled *The Art of the Pāl Empire in Bengal* was read by J. C. French, Esq., I.C.S. The Rt. Hon. The Earl of Ronaldshay, G.C.S.I., G.C.I.E., presided.

SOCIETY OF GLASS TECHNOLOGY.

The last meeting of the Society of Glass Technology for the session 1923-24 was held in Sheffield on June 18, the President (Col. S. C. Halse, C.M.G.) in the chair. Two papers were presented.

Some Remarks on the Erection and Operation of Modern Pot Furnaces, by Percival Marson. In the absence of the author this paper was read by Prof. W. E. S. Turner, D.Sc.

The author pointed out that the glass manufacturer, before constructing a pot furnace, which represented so heavy a capital expenditure, should have adequate plans prepared. A furnace builder who knew his business should be able to guarantee his furnace, but in any case it was desirable to have a technologist as intermediary in order that suitable specifications might be laid down and adhered to. Amongst other things the builder should study the nature of the ground upon which the furnace was to be erected, and he should construct an adequate foundation, providing also any necessary drainage and protection of the flues from ingress of water. The provision of suitable flue dampers with some form of indicator allowed of a more accurate regulation of the furnace during working. A small hole in the furnace above one of the pots served to give an indication, by observation of the issuing flame, of the state of combustion, so that correct conditions could thereby be attained. For a "full crystal" glass a furnace temperature of 1306° was sufficient, and nothing was gained by exceeding this, but for soda-lime glass a temperature of 1400° could be maintained with advantage. It was claimed that for the crystal glass a circular pot was better than an oval or egg-shaped one, since it was less likely to cause cords in the glass.

Note on an Unusual Type of Recuperative Tank Furnace, by F. W. Hodkin, B.Sc., and Prof. W. E. S. Turner, D.Sc. This paper was presented by Mr. Hodkin, who gave an account of observations made upon a recuperative tank furnace in operation at the Belinda Works of Messrs. Lax & Shaw, Ltd., Leeds. The observations were made as the result of an invitation extended by Mr. J. S. Shaw to Prof. Turner to inspect the furnace.

The main feature of interest was the method of recuperation of the secondary air. This air entered by arched passages situated beneath the bottom of the tank and above similar passages conveying the exit gases to the chimney flue. It then passed by means of vertical channels in the working end of the furnace to a space between an upper and a lower crown. After traversing the space between the crowns, the air entered the furnace through a series of ports which were placed so as to have the gas ports between them.

Producer gas was admitted, without preheating, through a gas-chamber connected with ports or burners opening into the melting end of the furnace. The flames traversed the whole length of the furnace, the products of combustion escaping through the vertical downtakes in the working end to the flues beneath the tank.

The batch was charged through an opening at the side of the furnace, and one big advantage claimed for the method of construction was that it permitted of working operations being conducted along the walls, not only of the working end, but also of the melting end, by the use in the latter of syphons.

The tank had a double bridge. In other words the bridge had three walls separated by cavities through which steam was blown for cooling purposes.

With gas at 700° C., and air at 720° C., the temperature of the glass in the melting end was 1460° C. The production of glass from the tank, which was not being worked at full capacity, averaged 80 tons per week for a consumption of about 60 tons of coal on the producers. This glass was worked by three machines, with feeders situated in the working end of the furnace, and by hands from four boots in the melting end. The designers anticipated a production of more than 120 tons of glass per week when working fully.

The President intimated that a party of members of the Society was visiting Belgium from July 7 to 12.

PHYSICAL SOCIETY OF LONDON.

JUNE 27.

The following papers and demonstrations were presented:—

The Electron Emission Constants of Metals, by PROF. O. W. RICHARDSON, F.R.S., King's College, University of London.

A Demonstration of *The Fluorescence of Transparent Fused Silica*, by DR. W. E. CURTIS, King's College.

A Demonstration of *A Selenium Photometer*, by DR. F. C. TOY.

A Method for Measuring very Small Capacities, by L. HARTSHORN, D.I.C., National Physical Laboratory.

A Demonstration of *A New String Galvanometer*, by PROF. ERNEST WILSON, King's College.

Proceedings at the meeting held on June 13, F. E. Smith, C.B.E., F.R.S., in the chair:—

On a Method for the Synchronous and Instantaneous Illumination of Objects Rotating or Vibrating at Very High Speeds, by DR. G. E. BAIRSTO, Royal Aircraft Establishment, Farnborough.

A method was described for the instantaneous and synchronous illumination of very rapidly rotating or synchronously vibrating objects.

It is capable of giving instantaneous photographic records, and gives a precision of the order of half a micro-second. It is much more precise and able to give a more intense spark than any contact breaker and coil method.

The Absorption and Scattering of γ-Rays, by DR. E. A. OWEN, MR. N. FLEMING and MISS W. E. FAGE.

The absorption and scattering of gamma rays from radium filtered through 23 mm. of lead have been measured in magnesium, aluminium, zinc, tin and lead.

On the assumption that the mean effective wave-length of the radiation employed is 0.021 A, the experimental results are consistent with the following statements:

When gamma-rays traverse matter, the characteristic radiations of the absorbing medium are excited.

The atomic fluorescent absorption coefficient of gamma-rays depends upon the wave-length of the incident radiation and the atomic number of the absorber according to the law $\frac{\tau}{\rho}\cdot\omega = K\lambda^3N^4$, which holds for X-rays.

The radiations which accompany this fluorescent absorption are the characteristic radiations of the K, L, M,...series of the absorbing elements.

The absorption of gamma-rays in light elements is due almost entirely to scattering.

The pure atomic scattering absorption coefficient is proportional to the atomic number of the absorber.

In addition to fluorescent and scattering absorption, a true absorption exists, the atomic coefficient of which is proportional to the atomic number.

Compton's formulæ, deduced from his Quantum Theory of Scattering, would account for the experimental results if the wave-length of the incident radiation were 0.020 A. Jauncey's formulæ would require the wave-length to be 0.029 A.

The Flow of Compressible Fluids, Treated Dimensionally, by W. N. BOND, M.Sc., University College, Reading.

The method of dimensions treatment that is applicable to the pressure gradient at a point in a system through which noncompressible fluids of finite viscosity are passed, is in this paper extended by means of the thermo-dynamical equations for gas flow to the case where appreciable changes in density of the fluid occur, but where no heat passes across the walls of the system. The theory is developed in detail only for the case of flow through a straight parallel-walled tube.

The theory is then tested by means of experiments in which water and air at high velocities pass through small tubes. The air in some experiments had a velocity of more than two-thirds of the velocity of sound in the air. The possibility of errors due to moisture, pulsating flow, heat conduction through the walls, and proximity to the entrance to the tube is considered, experimentally and by approximate calculation, and the errors are shown to be small in the present experiments. An error of attributed to the partial neglect of the variation of the variables over the transverse section of the tube. The value of the error varies in the way it might be expected to do, and is of the order that is expected by other considerations.

MINERALOGICAL SOCIETY.

JUNE 17.

Dr. H. H. Thomas, Vice-President, in the chair.

Papers read:—

PROF. MIKLOS VENDL: *The Chemical Composition and Optical Properties of a Basaltic Hornblende from Hungary.*

Complete determinations were made, all on the same sample of material, of crystals of a black hornblende occurring in volcanic tuff near Lake Balaton. The mineral is rich in titania, alumina, ferric iron, and alkalis, and the composition is expressed by the mixing of simple metasilicate molecules (including 14.62 per cent. H_2SiO_3) with aluminate (14.40 per cent. Mg Al_2O_4), and ferrate (4.32 per cent. Mg Fe_2O_4).

G. ABBOTT and W. A. RICHARDSON: *The Micropetrography of the Structures of the Magnesian Limestone of Fulwell.*

The structures of the magnesian limestone show a wide variety of forms ranging from simple spherical concretions to highly complex coral-like masses. The more complex types are built up by a combination of rods, tubes and bars. The microstructure shows more uniformity. The prevailing type is finely granular but crystalline. Where impurities or lines of pigmentation are present the matrix becomes quite microcrystalline as a rule, whilst on the borders of cavities there is a coarser growth. Banded pigmented forms show the same structure as banded chert. Spheroids have either a coralloid structure, or, if solid, are microcrystalline at the centre, with a radial crystallisation towards the surface. The microstructure by itself throws little light on the origin.

NOTICES OF BOOKS.

Schwefel und Stickstoffstudien (Sulphur and Nitrogen Studies), von DR. F. RASCHIG. Pp. 310. 1924. Leipzig and Berlin: Verlag Chemie G.m.b.H.

This monograph is the result of laborious investigations and researches extending over 30 years. These have not been exclusively confined to academic and purely scientific enquiries, but have assisted in the elucidation of the real problems met with in actual works' practice.

The scientist should concern himself with the difficulties encountered in industrial processes. On the other hand, the technologist cannot afford to ignore the advances made in pure science.

The volume includes 24 chapters, embracing articles on a variety of topics connected with sulphur and nitrogen compoundings. Mention may be made of the accounts of the action of nitrous acid upon sulphurous acid (his great work); a new oxide of nitrogen; the combination of nitrogen and iodine; the compounds of nitrogen with gold; monochloramine; hypo nitrous acid. Several papers are devoted to the various sulphonic acids of hydroxylamine, the oxidation and reduction and hydrazoic acid, and the preparation, properties and constitution of the polythionic acids.

Many chemists outside Germany will be glad to read this monograph containing so much of Raschig's work.

J.G.F.D.

A Short History of Chemistry, by ROSE STERN, B.Sc. Pp. VI. + 152. London: Messrs. J. M. Dent & Sons, Bedford St., W.C.2. 1924. 2s. 6d.

There are few good histories of chemistry, and hardly one can claim to be suitable for young readers. The attention of science masters and mistresses is therefore directed to Miss Stern's interesting little volume on the subject.

Her short history of chemistry briefly covers the whole story of the science from the earliest conceptions, tracing the developments up to the present time, and concludes with a chapter giving a fairly full description of modern ideas on the structure of the atom.

Obviously it would be difficult to go into much detail in a mere 152 pages, and only discoveries and theories of prime importance have been described. The early work and knowledge up to the time of Boyle has not received so good a treatment as the period following. The account of the progress made at the time of Priestley and Cavendish, including the generalisations and discoveries of Lavoisier and Scheele is particularly good. Indeed, none of the contents of the book can be criticised: the subject has been presented so admirably, and gives a clear idea of the gradual growth of chemical knowledge.

The illustrations add to the attractive-

ness of the book, which should appeal to boys and girls in a way that text-books seldom do.

J.G.F.D.

The Manufacture of Sulphuric Acid (Chamber Process), by WILFRID WLYD. Vol. II. Pp. XII. + 424. London: Gurney & Jackson, 33, Paternoster Row, E.C.4. 1924. 31s. 6d. net.

This volume of the new edition of Lunge's *Sulphuric Acid and Alkali Manufacture* gives a very detailed account of the "chamber" process, especially from the industrial standpoint.

In spite of recent advances in "contact" and other processes, the old chamber method still survives. It is still the object of further patents and improvements, and the latest and most complete information is contained in Mr. Wyld's volume.

Chapter I. deals at length with the construction of the lead chambers and towers, and the regulation of the reactions which take place therein. In Chapter II. an account is given of the methods for recovery of the oxides of nitrogen. The next chapter is concerned with the actual process and the chemical reactions. Then follows a description of the purification of the acid —removal of arsenic, selenium and nitrogen compounds.

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J.G.F.D.

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Latest Patent Applications.

13555—Coke, B. E.—Oxidation of alcohols and aldehydes. June 4.

13507—Coke, B. E.—Oxidation of derivatives of aromatic hydrocarbons. June 2.

Specifications Published this Week.

215880—Moseley, J. F. — Agents or assistants for detersive, scouring, bleaching, dyeing and like operations.

216192—Lamoreaux, W. F.—Process and apparatus for making sulphuric acid.

198332—Lamoreaux, W. F.—Manufacture of sulphuric acid.

216368—Farbwerke vorm, Meister, Lucius & Brunning.—Manufacture of ethyl chloride.

216450—Mathieson Alkali Works, Inc.—Manufacture of hypochlorites.

Abstract Published this Week.

214483—Titanium oxide.—Chemische Werke vorm Auerges, 11 Ehrenbergstrasse, Sommer, F. 47, Mommsenstrasse, Charlottenburg, and Ans, J. D., 2, Werftstrasse, all in Berlin.

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THE CHEMICAL NEWS,

VOL. CXXIX. No. 3352.

THE HYDROGEN OVERVOLTAGE OF METALS AND THEIR CHARACTERISTIC PROPERTIES.

PART II.—OVERVOLTAGE & MELTING POINTS.

BY EDWARD J. WEEKS, PH.D., M.Sc., A.I.C., F.C.S.

In a previous paper (*The Chemical News*, 1924, CXXVIII., 359) it was shown that the hydrogen overvoltage of a metal, as defined by Newbery, is not directly related to its valency. A table was given of the average overvoltage of some metals, arranged in order of their characteristic valencies.

Now Mott has previously pointed out that the overvoltage of a metal, when measured by the direct method (Caspari, *Zeitschr. Phys. Chem.*, 1899, XXX., 89). (The overvoltage is here measured by direct measurement of the potential difference between each electrode and a standard electrode whilst the current is flowing c.f. Newbery, and Sand and Weeks) (*loc. cit.*) bears a relation to its melting point. The higher the overvoltage was, the lower was the melting point of the metal.

Now on examination of the table in Part I. of this paper, it will be noticed that the metals divide themselves naturally into two groups. Those with an overvoltage between 0.50 and 0.60 in Group I., and those with an overvoltage of 0.30 and under in Group II. Antimony may be taken as the last metal in Group I. It is at once obvious that the first group metals are metals of low melting point, whereas the second group metals are metals of high melting point. Below is given a table in which the metals are arranged in order of their average overvoltages and their melting points.

TABLE.

	Metal.	Overvoltage.	Melting Pt.
Group I.	Mercury	0.69	-38° C.
	Bismuth	0.50	264° C.
	Thallium	0.54	303° C.
	Cadmium	0.50	321° C.
	Lead	0.61	326° C.
	Zinc	0.60	419° C.
	Antimony	0.54	630° C.
Group II.	Silver	0.23	960° C.
	Copper	0.31	1080° C.
	Gold	0.31	1061° C.
	Nickel	0.30	1484° C.
	Cobalt	0.21	1530° C.
	Iron	0.32	1600° C.
	Tungsten	0.35	2800° C.
	Rhodium	0.00	Over 3000° C.

We hence arrive at the following conclusion:—

The higher the melting point of a metal, the lower is its hydrogen overvoltage. The highest overvoltage is that of mercury, 0.69 of melting point -35° C., whereas the lowest overvoltage is that of rhodium, 0.00, whose melting point is somewhere over 3000° C.

The above results are for overvoltages in acid solution only. In a further publication it is hoped to consider overvoltages in alkaline solutions.

The Sir John Cass Institute,
Aldgate.
June 30, 1924.

SPIRO COMPOUNDS WITH REFERENCE TO FORMATION AND STABILITY.

PART II.—THE APPLICATION OF THE DIECKMANN REACTION TO ESTERS OF THE GLUTARIC SERIES, THE DIECKMANN KOMPPA REACTION, AND THE INFLUENCE ON STABILITY OF GROUPS OF HIGH MOLECULAR WEIGHT.

BY R. F. HUNTER, A.R.C.Sc., M.S.CHIM., F.C.S.

The action of sodium on ethyl glutarate, as is well known, was studied by Dieckmann himself (*Annalen*, 1901, CCCXVII., 27), who obtained a very small amount of oil insoluble in sodium carbonate and giving a blue coloration with alcoholic ferric chloride. Dr. Kon, with a view as to obtaining further information as to the conditions of formation of ring ketones from di-

basic acids, repeated Dieckmann's work, and extended the investigation to the esters of three other acids, namely, gem dimethylglutaric acid, cyclopentane, and cyclohexanediacetic acids, using sodium and potassium as condensing agents under suitable conditions. The difference in behaviour of the last three esters from the first was most marked. Ethyl glutarate reacts with sodium, but working up the product of condensation, it is found that the substance formed consists of an extremely viscous gum, soluble in sodium hydrogen carbonate but insoluble in ether and water, which evades all attempts to prepare the pure substance. The action of sodium on the other three esters, however, gives rise to well characterised products, and it was shown that their production was due to the production of the cyclic ketonic ester. Such a ketonic ester has in no actual case been isolated, but in experiments with ethylcyclohexane diacetate it was possible to isolate the cyclic ketone derived from the ester by the loss by hydrolysis of a carbethoxyl group, namely, cyclohexanespirocyclobutanone, the constitution of which was placed beyond all doubt by its oxidation to cyclohexane 1 carboxylic 1 acetic acid. The ketone is saturated and quite stable to permanganate, and is analogous to the cyclohexanespirocyclopropanone, which was obtained in the form of its semicarbazone by Thorpe, Beesley and Ingold (*Jour. Chem. Soc.*, 1915, CVII., 1080). Though stable to neutral permanganate, it is oxidised slowly by the alkaline reagent in the cold. The substance exhibits marked exhalation in molecular refraction. As well as this substance, there is formed a solid diketone, which is acid in character, gives a violet coloration with ferric chloride, and which was shown to be a 1:2 diketone. In the manner typical of 1:2 diketones, this substance was quantitatively oxidised by alkaline hydrogen peroxide to cyclohexane 1:1 diacetic acid, the substance being clearly cyclohexanespirocyclopentane 3:4 dione. The formation of the diketone can only be explained by assuming that the original cyclobutane ester undergoes fission by reduction in the strongly reducing medium in which it is formed with the production of an aldehyde ester from which the alcohol is at once eliminated with the formation of the diketone. The process, as will be seen, resembles the benzoin condensation of benzaldehyde.

When gem dimethylglutaric ester was subjected to the action of sodium or potassium, the reaction was similar, but differed in one important respect. In the first place there was found no trace of 1:1 dimethylcyclobutanone, and in the second place the yield of enolic material was much smaller. There would then appear little doubt that these differences are due to the smaller tendency on the part of the dimethylglutaric ester to pass into the ketonic ester from which the other compounds are derived, and to the greater instability of the cyclobutane ring in this case; this is quite in accordance with the original hypothesis of Thorpe, Beesley and Ingold. The diketone which is formed from the dimethylglutaric ester is in all ways analogous to the cyclohexane compound which has been discussed above. It is identical with 1:1 dimethylcyclopentane 3:4 dione, which was prepared by Thorpe from methyldiketoapocamphorate (*Jour. Chem. Soc.*, 1911, LXXXXIX., 2010). It was considered necessary to make certain that the possible formation of 1:1 dimethylcyclobutanone was not overlooked, on account of its high boiling point, which would not be very different from xylene, which was used in the reaction, and it was therefore decided by Kon to investigate the behaviour of cyclopentane diacetic ester towards potassium. The formation numbers for ketones from this ester and dimethylglutaric ester are nearly identical, but the spiro ketone would boil at a considerably higher temperature, and should be isolable with no difficulty. It was therefore significant that no trace of such a compound was found in the neutral portion of the reaction mixture. A semicarbazone was isolated from this fraction, but analysis showed that it was in all probability a ketone derived from the diketone by reduction.

Cyclopentanespirocyclopentane 3:4 dione was isolated from the oil insoluble in sodium hydrogen carbonate, but soluble in potash solution. The yield of this compound was larger than that of the corresponding dimethyl compound, but smaller than that obtained from cyclohexanediacetic ester. The new diketone was in every way analogous to its higher homologues, and was characterised by Dr. Kon by the formation of derivatives.

From the above it is clear that the cyclobutane ring is only able to survive the conditions of the Dieckmann reaction when it

is combined with a cyclohexane ring, as is shown by the fact that cyclohexanespirocyclobutanone is the only cyclobutane compound isolated in Kon's research.

In 1922, Thorpe, Dickens and Kon brought forward evidence to show that the deflection of the tetrahedral angle affects five-membered ring formation in the manner similar to that of cyclopropane ring formation (*Jour. Chem. Soc.*, 1922, CXXI., 1496).

The reaction examined was that by which Dieckmann prepared derivatives of cyclopentandione by the condensation of oxalic and glutaric esters in the presence of sodium. The reaction is capable of being represented in two ways, either (*a*)

$$(a)\ CH_2\ (CH_2CO_2Et)_2 + (CO_2Et)_2$$

$$CH_2 < \begin{matrix} CH\ (CO_2Et)\ CO \\ | \\ CH\ (CO_2Et)\ CO \end{matrix} + 2\ Et\ OH$$

or (*b*), in two stages, an oxalyl derivative being formed as an intermediate product.

$$(b)\ CH_2\ (CH_2CO_2Et)_2 + (CO_2Et)_2$$

$$CH_2 < \begin{matrix} CH\ (CO_2Et)\ COCO_2Et + EtOH \\ CH_2CO_2Et\ (1) \end{matrix}$$

$$\rightarrow CH_2 < \begin{matrix} CH\ (CO_2Et)\ CO \\ | \\ CH\ (CO_2Et)\ CO \end{matrix} + Et\ OH$$

It was clearly necessary to ascertain the course of the reaction, and this was done by Kon, Dickens and Thorpe. It is clear, for instance, that any tendency to five-membered ring formation, due to deflection of the tetrahedral angle, would be greater in a reaction of the first type than in a reaction of the second type, because in the former the necessary alteration in valency direction would be borne by both carbon atoms of the oxalic group, and in the second case the whole change would be borne by a valency of one carbon atom. The experiments demonstrated clearly that the reaction was of the second type (*b*), and in the case of the simplest member it was actually possible to isolate the oxalyl derivative (1). This discovery also led to the explanation of some remarkable facts in the literature of the subject. Dieckmann found that the greatest yield was obtained when ethyl glutarate was used, and a diminished yield was obtained with ethyl β methyl glutarate, and a poor yield resulted when ethyl gem dimethylglutarate was used. Now it will be noted that if the reaction were of the first type, then the greatest yield would be obtained from the dimethyl compound in which the tetrahedral angle difiers only from the angle of the cyclopentane ring by a few minutes of en arc. Now the greatest yield of condensation product is given by the glutaric ester itself, and it therefore follows that in the oxalyl derivative (1) the carbon atoms which are to join to form the five-membered ring are nearer together than in any other member of the series, and it follows that this effect can only be produced by the alteration of the normal angle to a value approaching that of the cyclopentane ring, and this result is brought about by the presence of the oxalyl group on the alpha carbon atom.

The effect produced by a further deflection of the tetrahedral angle due to the presence of gem groupings or ring complexes, would clearly produce an overlapping effect in the positions of the two carbon atoms which are required to link in order to produce five-membered ring formation, with the result that the greater the deflection the greater the difficulty experienced in closing the ring until a stage is reached where ring closure becomes impossible.

The experimental results showed clearly that as regards the series, as the tetrahedral angle decreases the yield of five-membered ring condensation product decreases.

It would appear that in this series, the carbon atoms which are to join to form the five-membered ring have reached positions of closest proximity in the oxalyl derivative of the unsubstituted glutaric acid derivative, and that in the successive members of the series the distance between these two carbon atoms increases through overlapping. Certain other facts arose out of the investigation which could only be explained on the above lines. For instance, the increasing deflection of the angle which leads to the increasing separation of the two carbon atoms required for ring closure must tend to bring the two carbon atoms required for four-membered ring formation into closer proximity. If the compound under investigation lends itself equally well to four and five-membered ring formation, it is to be expected that in those cases where overlapping has separated the carbons re-

quired for five-membered ring formation to a distance which prevents the reagent used from joining them, as in, for example, cyclohexane diacetic ester, evidence will be available to show that some, at any rate, of the four-membered ring compounds will be produced in the reaction. The oxalyl derivative is a compound of the type described, for not only can it be transformed into the five-membered ring, but it can also be transformed into the four-membered ring (*J.C.S.*, 1922). Oxalyl derivatives of this kind are, as it is well known, readily hydrolysed, and then pass into the monocarboxylic ester in the manner indicated. Therefore, it is to be expected that if any of the four-membered ring derivative is formed in the diethylglutaric acid and cyclohexanediacetate condensations, it will be found as in the steam distillation products. The work of Kon, Thorpe and Dickens was conclusive in so far as they showed that a small quantity of the four-membered keto ester was produced in the condensation of methyl $\beta\beta$ diethylglutarate and methyl oxalate by the Komppa modification of the Dieckmann reaction, but unfortunately all attempts to isolate a similar compound in the cyclohexanediacetate series failed.

Particular interest attaches itself to the investigotion of Prof. Thorpe and Dr. Birch. With regard to the Guareschi reaction, attention has been drawn to the relative stability of the cyclohexane derivative as compared with the dimethyl compound, due to the alteration in the tetrahedral angle. It was found that the cyano acid readily underwent fission to the hydroxy acid, whereas under the same conditions the cyclohexane acid was unchanged. This method, therefore, appeared likely to be useful for the purpose of determining the relative stability of similarly constituted structures, and this proved to be the case, for it was found that the reaction by which the dicyanocarboxylic acids were prepared was a general one, and that these compounds and their fission products can always be prepared from the relevant imide under special conditions. The method involved the preparation of the Guareschi imide, its conversion into the ring imide by the aid of bromine, an dthe hydrolysis of this to the dicyanocarboxylic acid (2) when it is stable, or to the hydroxy open chain acid where ring fission occurs.

$$\begin{matrix}CH_3 \\ CH_3\end{matrix} > C < \begin{matrix}C\,(CN)\,CO_2H \\ | \\ C\,(CN)\,CO_2H\end{matrix} \qquad (2)$$

Clearly, by employing a selected number of many ketones which yield Guareschi compounds, a large field is opened for the study of ring structures, differing only in the character of the groups attached to the β carbon atom, and therefore well suited for the purposes of comparison. The discovery of the new method was of importance for two reasons,. firstly because it is more sensitive than that which had previously been used in the laboratories of the Royal College of Science which involved the study of the cyclopropane acids, a comparison which was strictly limited in application save in the case of the gem dimethyl compounds which yield terebic acid. It was not found possible to isolate any definite products owing to the deep-seated degradation leading to the formation of much free carbon involved in ring fission, and secondly, it provided a means whereby it was possible to investigate the behaviour of groups of molecular weight greater than that of methyl on the stability of ring structures under discussion. In the earlier work which has already been discussed to some length, a hypothesis was established regarding the effect of angle change caused by the definite alteration of the tetrahedral angle due to the inclusion of two of the valencies of the β carbon atom in a ring complex. Experiments were carried out by Deshapande and Thorpe (*Jour. Chem. Soc.*, 1922, CXXI., 1430), which showed that the effect on the next carbon atom in a chain of two linked carbon atoms is greater than that of one. Thus the behaviour of the gem diethyl compound as regards stability, and also as shown by the occurrence of tautomerism between the hydroxy derivative and its open chain form, indicated that the gem diethyl group exercised an effect on the tetrahedral angle which was between that caused by the dimethyl group and that produced by the cyclohexane ring.

Thorpe and Birch therefore examined the stability of the dicyano-dicarboxylic acids

$$CRR' < \begin{matrix}C\,(CN)\,CO_2H \\ | \\ C\,(CN)\,CO_2H\end{matrix} \qquad (3)$$

from diethyl ketone, methyl-n-hexyl ke-

tone, cyclopentanone and benzyl methyl ketone, and found that these substances were broken down into open chain acids.

OH CRR′ C (CN) (COOH) CH (CN) COOH
(4)

Clearly, then, none of these acids approaches in stability that derived from cyclohexanone and the attachment of groups of high molecular weight and those having long carbon chains does not affect the tetrahedral angle to an extent greater than that exercised by the cyclohexane complex. The method, unfortunately, did not make it possible to distinguish between the compounds which undergo fission, because, under the experimental conditions the ring is either completely destroyed or unattacked. Or, to put it another way, the reaction is so rapid that it does not appear possible to devise any series of experiments by which its rate might be determined.

A point of interest in this work was that, having established in the dimethyl and diethyl series that the volume of a carbon atom attached to one of the valencies of a carbon atom is increased by the linking of another carbon atom to it, but that this volume effect is so small even when six carbons are linked, as in the methyl-n-hexyl series compared with that produced by the cyclohexane ring, it was decided to ascertain whether any change in the tetrahedral angle could be detected by replacing one of the hydrogen atoms of the cyclohexane ring by a methyl group. Ring imides were therefore prepared from 4 and 3 methylcyclohexanone, and it was found in each case that the presence of the methyl group destroyed the stability characteristic of the unsubstituted ring dicyano acid, and that the hydroxy acids were the sole products formed by the reagent used.

Highbury New Park.
May, 1924.

British Empire Exhibition.

PARTICULARS OF EXHIBITS IN THE CHEMICAL HALL AT THE BRITISH EMPIRE EXHIBITION.

THE WALPAMUR COMPANY, LIMITED.

In order to conform to the architectural features of the building in which it is placed, the Walpamur Company have designed their stand to represent part of the interior of a Baronial Hall, and have provided furniture and fittings consistent with this scheme. The walls have been panelled throughout—those in the outer, or main, portion being decorated with buff coloured Walpamur water paint and panelled in grey oak, whilst the inner portion, or recess, which has a deep dado of grey oak, has been treated with Muromatte Flat Oil Paint, jade green in colour, and with the strapping of the panels picked out with gold studs.

A feature of the scheme is the frieze under the oak cornice, the panels of which are decorated with the coats of arms, in colour, of each city and town in which the Company has established a branch.

The wooded boundary partition has also been included in the scheme, and has been treated with Duradio Gloss Paint, in panels of pearl grey and azure blue. The floor is composed of black and white squares.

All the paints and colours used were manufactured by the Company at their works in Darwen, Lancashire, and have been applied under practical conditions. The result shows how the smaller homes of to-day may, with more imposing buildings, lend themselves to practical and artistic treatment.

It is an exhibit that should not be missed.

GENERAL NOTES.

WORLD'S CEREAL CROP PROSPECTS.

According to information collected by the International Institute of Agriculture and published in its Crop Report for June, in most parts of Europe temperature and fine weather alternating with rain-storms prevailed during the latter half of May, and proved favourable to cereal growth, thus partially repairing the damage caused by the inclement season in the northern and central regions. At the beginning of June crop conditions were almost everywhere better than those of a month earlier, although the situation in Northern Europe generally and in parts of Russia was less satisfactory than at the same period in 1923. Prospects in Danubian and Balkan countries were, however, more promising. Persistent drought and hot winds in South-

ern Italy, in parts of Spain, and in North Africa have been injurious and have caused premature ripening of crops.

In North America crop conditions at the beginning of June were generally below those of June, 1923, while growth is backward, especially in Canada. The area sown with spring wheat in the United States is less than last year's, though the decrease is not quite so marked as had been expected. Some decline has also taken place in the areas under rye and barley. For Canada, the figures of areas sown with cereals will not be available before July 10.

For wheat, estimates from five countries usually growing about one-fourth of the world's yield, afford an aggregate of 745.1 million centals, as compared with 816.4 million in 1923, thus showing a forecasted decrease of 8.7. The most serious decline is in the United States, where the outlook is for a crop of 55.5 million centals less than last year's, and 112.7 million below the average of the previous five years; in Spain and in India results appear likely to be less favourable than in 1923, but better than the five years' average yields; Belgium expects crops rather larger than in 1923 and over their previous average out-turns.

These data deal with a number of countries too limited for any authoritative opinion on the season's aggregate results; but taking into account the reduced acreage *and the present aspect of spring-sown* crops generally, there is good reason to believe that the Northern Hemisphere wheat crop of 1924 will, as a whole, be inferior in quantity to that of last year.

For rye, barley and oats, the few data yet available indicate a smaller aggregate, but the forecasted yields represent only a very small proportion of the world crops.

Taking into account the early estimates of areas sown, and of crop conditions at the beginning of June in those countries whence no figures are available, it would seem probable that, generally speaking, the yields of rye, barley and oats in 1924 may be less than last year's.

Further telegrams received at the Institute give the following information:—

In the United States, winter wheat *shows an improvement, and spring wheat* has benefited from the rains. Likewise for oats prospects are now more favourable.

In Hungary the warm and rainy weather of the first half of June proved propitious for the cereal crops.

With regard to Russia, the most recent reports available state that the drought in the south, in the south-east, and in the Lower Volga Region, together with the excessive rains in several of the northern regions, resulted during the latter half of May in lowering the cereal crop condition, which, in fact, at the beginning of June was reported as being below the average and less favourable than at June 1 of last year.

CHEMICAL IMPORTS IN BRITISH MALAYA.

During the first three months of 1924 British Malaya imported 407 tons of acetic acid, valued at £28,877. Of this, 374 tons, valued at £26,622, came from the Continent of Europe, and 28 tons, valued at £1,842, from the United States of America.

Imports of sulphuric acid were 114 tons, valued at £1,733, of which 111 tons, valued at £1,491, came from Japan. Other acids imported amounted to 44 tons, valued at £2,085.

Disinfectants imported amounted to 19,156 gallons, valued at £3,884, of which 17,194 gallons, valued at £3,536, were exported from the United Kingdom. British possessions were responsible for the whole amount of saltpetre imported—57,267 lbs., valued at £989. Of the total import of 8,491 cwts. of soda and sodium compounds, the United Kingdom provided 7,933 cwts., valued at £6,178. Other chemicals to a quantity of 27,045 cwts. and a value of £29,017 were also imported, more than 80 *per cent. of these coming from either the* United Kingdom or some other part of the British Empire.

BENTONITE, OR COLLOIDAL CLAY.

Attention has been directed during the last few years to a peculiar clay found in the western parts of the United States and Canada, called bentonite. The clay was first described from the State of Wyoming, and has been found also in other States of the Union, and in the provinces of Manitoba, Saskatchewan, Alberta, and British *Columbia, in Canada.* The Mines Branch of the Department of Mines of Canada has recently made a survey of the known bentonite deposits with a view to determining the extent to which the clay occurs in Canada.

It has been found that bentonite is pretty widely distributed in the upper sections of the Cretaceous rocks which cover the greater part of the Prairie Provinces, and that many of the sandy or shaly beds in this series of rocks are bentonite in varying degree. The sticky "gumbo" soils of the west owe their character to the presence in them of bentonite, which swells up when wet and forms a pasty mass that makes the prairie roads at wet seasons almost impassable. The University of Alberta is at the present time conducting experimental work in the improvement of highways by counteracting the evil effects of bentonite.

The bentonite beds of the Canadian West range in thickness from a few inches to as much as 14 feet. The latter thickness is exceptional, but several deposits measuring 6 to 8 feet are known. The deposits which probably offer the best possibilities for immediate development occur in southern Saskatchewan and southern British Columbia, where beds are found quite close to railway transportation. No production from any of the deposits has yet been made, owing to the lack of a market. In the United States, however, two companies are now marketing bentonite; one of these produces only crude clay, and the other both crude and powdered material. These companies report that the market is small as yet, but is growing steadily each year, and that an encouraging interest is being manifested in the possibilities of the clay by the most varied industries. In 1921, the Mines Branch arranged the shipment of 5 tons of Alberta bentonite to the Imperial Mineral Resources Bureau, 2, Queen Anne's Gate Buildings, London, for research purposes and for distribution in British industries. It is understood that the Bureau still has a quantity of the clay on hand.

Bentonite in the dry state looks much like any other clay. It is only when it is wetted that its peculiar physical properties become apparent. The name bentonite was given about twenty-five years ago to the clay from a bed that occurs in rocks of Upper Cretaceous age (Fort Benton series) in Wyoming, and attention was drawn to the material on account of its excessively sticky nature and its high water absorption. It possessed, in short, the physical attributes of what are now called "colloids." Briefly, bentonite is a clay substance, the individual particles of which are so small that they are invisible even under the highest powered microscope: they are not crystalline like ordinary clay particles, and when mixed with an excess of water form what are called "hydro-sols"—that is, permanent suspensions, or dispersions, from which the clay will not settle out, even if allowed to stand indefinitely. By virtue of the relatively enormous surface presented by the particles, bentonite possesses great absorptive power, and the dry clay will absorb many times its volume of water, swelling up to a sticky, jelly-like mass. The particles have the property of absorbing chemical compounds also, such as salts, dyes, etc., out of solution, and of effecting base exchange between salts of the alkali and alkali earth groups.

These properties have suggested a very wide field of usefulness for bentonite in industry. Some of the more important of these uses are: as an absorbent of dyes and colours; to increase the strength of cements and plasters; as a suspending agent for enamels and glazes in the metal enamelling and ceramic industries; as a bonding agent in crucible bodies, electrical and chemical porcelain and abrasive wheels; as a dewatering agent for petroleum, gasoline and oils generally, as well as for air and gases; as a mordent and as a base for lake colours in the dye and colour industry; as an accelerator and stabiliser of emulsions of various types, and in the preparation of asphalt, coal tar residues and pitch emulsions; as an absorbent of nitro-glycerine in the manufacture of dynamite; as a filler material for fertilisers; and for paints, rubber, and moulded composition products of various kinds; as a suspending agent in core washes for foundry work, and as a bonding agent in moulding sands; as a sticking or spreading agent in insecticidal sprays and dusts, and to increase the wetting power of cattle dips; as an ingredient of lubricants; in cold water paints or distempers; as an ingredient of adhesive pastes; as a sizing agent for textiles, cordage, etc.,; as an ingredient of crayons, indelible pencil leads and pastel colours, and of printers' inks; for increasing the retention of china clay in the manufacture of paper, and for removing the carbon black particles in the de-inking of newsprint; to remove the impurities from petroleum, gasoline and lubricating oils, as well as from packing-house products and vegetable oils (acid-treated clay); to replace whiting in putty; as a source of pure colloidal silica, or silica gel; as a detergent in

soaps and scouring compounds; as an ingredient in stove polish; in pharmaceutical products, cosmetics, facial clays, etc.

The above list by no means exhausts the many suggested uses for bentonite. Thus far, important commercial utilisation has been confined to the paper and oil industries, the latter being by far the largest consumer. The clay in this case, while probably more or less identical with bentonite, is variously termed halloysite or otalite, and is found in southern California: large quantities have been used by the Pacific Coast oil refineries, the clay being first treated with acid.

The Mellon Institute of Industrial Research of the University of Pittsburgh has issued the second supplement to Bulletin No. 1 (Bibliographic Series). This contains a list of the books, bulletins, journal contributions, written by members of the Institute, and patents taken out by them during the calendar year 1923. It shows that a surprisingly great activity is being conducted by this Institute in the field of industrial science.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE FARADAY SOCIETY.

JULY 7, 1924.

Papers read:—

A Note on the Conduction of Heat Down the Necks of Metal Vacuum Vessels containing Liquid Oxygen, by G. R. D. HOGG, B.A. (Oxon.).

Griffiths has described the metal vacuum vessel used for the storage of liquid oxygen, and has discussed briefly the various causes to which thermal leakage into the interior of such vessels may be attributed. This question has also been dealt with in the Report of the Oxygen Research Committee. These discussions show that the heat which enters cold liquids stored in vacuum vessels is transferred from the outer shell by three principal agencies, conduction through the residual gas in the vacuum space, radiation across the vacuum space and conduction down the walls of the inner neck which usually forms the only solid connection between the inner and outer vessels. It is possible by methods indicated by Griffiths to calculate approximately the amount of heat which will enter by the first two agencies, but the amount traceable to the third agency is difficult to estimate, and there are considerable differences of opinion as to its magnitude.

In neither of the sources quoted is any attempt made to calculate the heat entry down the neck, and experimental data available are meagre and their accuracy doubtful. Both accurate calculation and experiment are rendered difficult by the fact that a stream of cold gas from the interior of the vessel and by abstracting heat from the inner walls of the neck of the vessel materially affects the temperature gradient, and therefore the flow of heat, in the neck. The magnitude of this stream of gas, and hence its cooling effect are, of course, directly proportionate to the total amount of heat entering the vessel, by whatever means, in unit time, and therefore depend not merely upon the size of the neck but also upon the other dimensions of the vessel.

Approximate methods are now given for calculating the "neck loss" of metal Dewar flasks containing liquid oxygen. The methods may also be used for determining the most suitable dimensions for the inner neck of a metal Dewar flask, the other dimensions of which are known.

The Mechanism of Setting of Calcium Sulphate Cements, by C. L. HADDON, A.I.C., A.INST.P., M.Sc.

Though the nature of the chemical processes in the setting of calcium sulphate cements has been known since the time of Lavoisier, no completely satisfactory explanation of the physical processes involved has yet been put forward, the difficulty being that each authority has endeavoured to explain the hydration of every variety of calcium sulphate to dihydrate by one all-embracing hypothesis, and in every case, facts not explicable by the particular hypothesis have prevented any explanation being generally accepted. The object of this paper is to put forward an explanation which covers the known facts.

Calcium sulphate cements are chiefly manufactured from gypsum. On heating under manufacturing conditions, gypsum loses three-fourths of its combined water at about 130° C., with the appearance of "boiling." At 160-170° C. the remaining water is almost all lost, and anhydrous calcium sulphate with a little hemihydrate is left. This product is "soluble anhydrite." More intense and prolonged heating produces more perfect dehydration. Above

1000° C. decomposition of the calcium sulphate occurs.

The stable form of calcium sulphate in contact with water at ordinary temperatures is the dihydrate $CaSO_4 2H_2O$, and both the hemihydrate and anhydrous salt, on mixing with water, dissolve and reprecipitate as the less soluble dihydrate. If the rate of hydration is sufficiently rapid, a paste of burnt gypsum and water sets to form an adherent mass, and the use of such cements has been known for centuries. This absorption of water occurs also on exposure of anhydrous calcium sulphate to the atmosphere, hemihydrate being formed. With very fine particles such as in "soluble anhydrite," a few weeks in damp weather is sufficient for complete conversion into hemihydrate.

Plaster of Paris is almost entirely hemihydrate. With water, it sets to a hard mass in ten to twenty minutes, and its rapid setting prevents its being mixed with water by means of a trowel. It is usually stirred into a thick paste with water, and the thick cream produced poured into a mould. The plaster (sp. gr. 2.7) is generally mixed with about half its weight of water. The density of dihydrate is 2.31, thus if neither expansion nor contraction occurred in the apparent volume of the mass, a mixture of two parts by weight of plaster with one of water would produce 41 per cent. of voids in the final dry mass, and the reaction,

$$2CaSO_4.H_2O + 3H_2O = 2CaSO_4.2H_2O,$$

results in a decrease in true volume of 7.7 per cent. Actually there is a very appreciable increase in apparent volume, a property on which the commercial use of plaster for making casts depends. Van't Hoff, by means of a pyknometer, showed there was actually in setting a steady decrease in truo volume, followed by a slight expansion. Davis considers this to be due to the transition of an unstable β dihydrate to the stable α or monoclinic form.

The completely anhydrous salt is found a sthe mineral anhydrite. On mixing with water this hydrates very slowly, and the dihydrate formed is not adherent.

Intermediate in setting properties between these two extremes is gypsum heated to 500° C. and finely ground. Its water content varies, but 0.5 per cent. is a common figure. Its setting speed depends on the fineness of grinding and the amount of hemihydrate present, the time being of the order of six hours to acquire a tensile strength of 80 lb. per square inch. This speed is sufficiently slow to enable the plaster to be mixed with water by means of a trowel, and thus the proportion of plaster to be mixed with wthmarf dwolynup hmsc to water can be made considerably greater than with plaster of Paris, resulting in the production of a much stronger cement. It expands slightly on setting, but much less than plaster of Paris.

Le Chatelier claimed that on setting, the deposited dihydrate was in the form of spherulitic crystals, and the interlocking of these conferred on the mass its mechanical strength. Owing to the smallness of the crystals, he was unable to prove this in aqueous solutions, but in solutions of the hemihydrate to which alcohol had also been added and in which calcium sulphate is less soluble than in water, he obtained proof of the formation of such crystals. Von Weimarn showed that the nature of a precipitate depends on the solubility of the precipitate and the degree of supersaturation at the moment of formation. Great supersaturation yields gelatinous precipitates which subsequently crystallise. This may be classified as Type I. With medium supersaturation, spherulitic crystals are obtained (Type II.), while slight supersaturation results in the formation of well-defined single crystals (Type III.) The less the solubility, the greater is the tendency to form a gelatinous precipitate, and the smaller the supersaturation, the longer the time for complete precipitation and the larger the crystals formed.

There seems little doubt that the process of setting consists in the first place of the solution of plaster followed by its deposition as less soluble dihydrate. Ostwald and Wolski, and later Neugebauer, examining plasters containing much hemi-hydrate, found that on mixing with water there was temporarily a large increase in viscosity.

The true explanation appears to be that of Desch, who instanced the practical use of sodium thiosulphate solutions in imitating the action of frost on rocks. Here the growth of crystals results in a very great disintegrating force corresponding to the action of water on freezing, though in this case the volume of the solid deposited is less than that of the original liquid. The apparent expansion is due to the crystal growing in its true crystallographic form

rather than that of the cavity it occupies. It has been shown that set plaster is twice *as strong wet as when dry*, and the expansion of plaster kept thoroughly wet is much greater than when the mixed cement is allowed to set in a warm dry room and occasionally moistened. Thus the weaker the cement during setting the greater is the expansion. This result would be explicable if the expansion was due to crystal thrust.

The Vapour Pressure of Tellurium, by J. J. DOOLAN and J. R. PARTINGTON.

The vapour pressure of sulphur has been determined in various ways, and at least one determination of that of selenium has appeared. The vapour pressure of tellurium, however, has, apparently, not previously been measured, and an attempt has been made to determine its value, at least approximately.

The method employed was essentially that used by von Wartenberg in his investigation of the vapour pressures of metals. In this a measured quantity of inert gas is passed in a steady stream over the heated metal. The loss in weight of the metal was obtained at three fixed temperatures, at least three rates of flo wof gas being used at each temperature. From the relation

$$\frac{\text{mols. vapour}}{\text{mols. vapour} + \text{mols. gas}} \text{ the pressure of}$$

the element was obtained for each rate of flow, and by plotting these the pressure for zero rate of gas streaming was obtained for each temperature.

The quantity of gas used was determined by measuring the rate of flow and the duration of an experiment.

Nitrogen was chosen in preference to hydrogen as the inert gas because, although tellurium nitride has been prepared, it cannot exist above 200° C. On the other hand, if hydrogen were used, it is quite likely that traces of hydrogen telluride would be formed and vitiate the results.

Its flow was controlled with great accuracy by means of a venturimeter. The quantity of gas passing in each experiment was, therefore, exactly determined by the rate of flow and the time of duration of the experiment.

A silica boat contained in a silica tube was used to hold the tellurium, and back diffusion of the vapour was prevented by causing the gas to force its way through a tightly fitting plug, of boked fireclay, or, later, of uralite which had been previously maintained at a bright red heat.

Instead of having the thermocouple outside the tube, as in von Wartenberg's work, it was inserted in a silica sheath which fitted tightly into another resistant plug in the silica tube. In this way, during the passage of gas, the silica boat was enclosed in a tiny chamber in the middle of the heating zone of the electric furnace. By using a long silica tube the great advantage was obtained of having its ends quite cool. Thus, by attaching the inner plug to the weighed boat by a hook of nichrome wire and by affixing a second and similar plug to the thermocouple sheath, it was possible to draw the hot boat into a cooler part of the tube at the conclusion of an experiment and so allow it to cool in an atmosphere of nitrogen, without waiting for the whole furnace to cool before being able to withdraw and weigh the boat.

The coolness of the end also made luting and unluting a simple matter, so that the rate of flow of gas was readily checked, and the possibility of the development of an undetected leak obviated. Between experiments a current of gas was maintained for some minutes in order to remove any tellurium which had condensed on the plug or elsewhere in the heated region. The necessity for this procedure was pointed out by von Wartenberg, who found that failure to do so gave results which became lower owing to the now partly satnrated gas taking up less tellurium from the weighed boat.

The results were given in a table.

Cryoscopy in Sodium Sulphate Decahydrate, by E. E. TURNER and W. H. PATTERSON.

Cryoscopic and conductivity measurements have shown that the nitroprussides are derived from the acid $H_2Fe(CN)_5NO$, and not $H_4Fe_2(CN)_{10}(NO)_2$. Burrows and co-workers have further shown that ferrocyanides and complex oxalates also possess simple formulæ. The molecular weights of a number of sodium salts have now been determined, using sodium sulphate as cryoscopic solvent. The results of Löwenherz have, in general, been confirmed, and his experimental method has been adopted with only slight modification.

The depression of the transition point of

sodium sulphate produced by carbamide was found to be not strictly proportional to the concentration, a fact not recorded by Löwenherz. The deviation from proportionality was, however, insufficiently large to affect conclusions drawn in connection with the molecular complexity of solutes in general, since comparative, not absolute, molecular weights were required.

For K, the depression constant, the value 32.5 has been taken, partly from the results of the present work and partly from the results of previous workers.

The general reliability of the method was tested by determining the molecular weights of a number of organic compounds and of simple sodium salts. It was found necessary, in order to obtain sharp thermometric readings, to cause rapid initial crystallisation of the dodecahydrate from mixtures, this being effected by using a water-cooled air-jacket. Poor results were obtained when the jacket was kept at about 30°. In no case was the mixture allowed to supercool more than 0.3°.

Abnormal results were obtained for the molecular weights of sodium oxalate and borax. The low result for the former substance has been shown not to be due to solubility effects, whilst the molecular weight obtained for borax is in good agreement with the value obtained by Boutaric, Chauvenet, and Nabot.

The molecular weights obtained for sodium nitroprusside, ferrocyanide, aluminioxalate, ferrioxalate, and chromoxalate agree with those obtained by the measurements in aqueous solution referred to above.

Determinations made with sodium salts of d-tartaric and racemic acids show that racemic compounds do not exist in solution under the given conditions, although the latter would appear to be favourable for the persistence of racemic compounds derived from sodium.

The Catalytic Decomposition of Hydrogen Peroxide Solution by Animal Charcoal: The Production of Highly Active Charcoals, by J. B. Firth, D.Sc., F.I.C., and F. S. Watson, M.Sc.

Ordinary blood charcoal which has been previously heated to 120° C. shows only moderate catalytic activity in the decomposition of hydrogen peroxide solution. The catalytic activity is considerably increased by previous heating in a vacuum at 600° and 900° C., and is still further increased by previous sorption of iodine and subsequent complete removal of the iodine. It is shown that the activity of an activated charcoal consists of two types, one of which is very rapid and is termed α activity, and only exists for a few minutes, and a second type of activity, termed β activity, which may persist for several hours. In ordinary blood charcoal which has not been subjected to activation treatment, the α activity is absent. It is also shown that the introduction of iron into sugar charcoal considerably increases its activity.

In the present communication the behaviour of animal charcoal of various degrees of purity, and various degrees of activity has been studied. One of the objects which the authors had in view in this series of experiments was to obtain the maximum degree of activity by the methods already described.

The animal charcoal used in the first series of experiments was an unpurified commercial variety as supplied by Merck. The charcoal was repeatedly digested with boiling water until all water soluble material had been extracted. The resulting product, on ignition, gave 83.6 per cent. of ash. The ash consisted mainly of calcium phosphate, and a small amount of iron. The resulting charcoal was then very finely powdered and treated by one of the following methods:—

I. The finely divided charcoal was thoroughly dried in an air oven at 120° C.

II. The finely divided charcoal was introduced into a quartz flask, and heated in a vacuum for two hours at 600° C., allowed to cool in a vacuum, and the required amount of the charcoal rapidly weighed out.

III. As in II., except that the temperature of activation was 900° C.

IV. A quantity of the charcoal activated as in II. was treated with N/10 iodine solution in chloroform, in the proportion of 25 cc. of the solution per gram of charcoal, for twenty-four hours. The charcoal was then filtered off, transferred to a silica dish, and gently heated until practically the whole of the iodine had been volatilised. The charcoal was then shaken with an alcoholic solution of potassium hydroxide, and then boiled with distilled water until, on filtering, the filtrate showed no opalescence with silver nitrate solution. The resulting char-

coal was finally heated in a vacuum, in a quartz flask at 600° C., for two hours, and the required quantity of charcoal rapidly weighed out after cooling to room temperature.

V. Finely divided charcoal was first treated as in III., and then as described in IV., except that the final heating was carried out at 900° C.

The catalytic activity of the charcoal, after treatment by each of the above methods, was then determined. The experimental details were as already described. The hydrogen peroxide solution used contained 242.5 cc. of available oxygen per 25 cc. of solution. 0.25 gram of the charcoal and 25 cc. of the hydrogen peroxide solution were used for each experiment; the temperature of experiment was 18° C.

It was shown that the catalytic activity of purified animal charcoal is considerably increased by previous heating in a vacuum at 600° C. and 900° C. Previous sorption of iodine from solution, followed by complete removal of the iodine from the charcoal and finally heating in a vacuum increases the activity still further and gives rise to highly active charcoals.

The increased activity produced by the above methods is associated by an increase in the bulk of the charcoal.

Animal charcoal has been activated to such an extent that 80 per cent. of the available oxygen was evolved in one minute from a solution of hydrogen peroxide (approx. 10 vols.) by the introduction of 1 per cent. of charcoal and in another case 98 per cent. of the available oxygen was evolved in six minutes.

A repetition of the iodine and beat treatment at 900° C., for two, three and four times respectively, produced no appreciable increase in the catalytic activity towards the hydrogen peroxide solution, although the volume occupied by 1 gram of the charcoal progressively increased.

After the fourth sorption and expulsion of the iodine, on the addition of alcohol for the final washing of the charcoal, a vigorous reaction took place and aldehyde was produced in considerable amount.

The heat effect produced by the reaction has been determined for each type of experiment.

The Electrodeposition of Manganese—Part II., by A. J. ALLMAND and A. N. CAMPBELL.

It has been shown that pure electrolytic manganese can be obtained by the use of an electrolyte containing manganous sulphate and ammonium sulphate, employing a diaphragm cell, platinum anodes and a rotating cathode. Both purity of deposit and current efficiency depend essentially on careful regulation of the H· ion concentration within comparatively narrow limits. For a pure deposit, a low cathodic current concentration is desirable. As regards the optimum conditions for current efficiency, our experiments indicated that the best temperature is 30° C., and the most suitable cathodic current density 10 amps./d.m.^{2}.

This point, however, was uot quite settled, and further experiments, described in the present paper, were undertaken to decide the matter and also to see whether the physical nature of the deposit, which was distinctly unsatisfactory, could not be improved.

Fedotieff has published some results on this subject, using solutions of manganous chloride and manganous sulphate without the addition of the ammonium salt, and consequently found that the resulting cathodic deposits were highly basic. In his case they only contained 65-70 per cent. of metal.

The best conditions for the electro-deposition of pure manganese consist in the electrolysis of a solution containing manganous and ammonium sulphates (the catholyte) separated hy a diaphragm from the anolyte (ammonium sulphate solution), the H· concentration being kept at 10^{-6} to 10^{-8} by the regulated addition, as required, of sulphuric acid or of ammonia. The temperature is 30° C. and the current density at the cathode 10-15 amps./d.m.^{2}. The rotating alumnium cathode has a burnisher lightly pressing against it.

Electrolyte manganese was found to contain a considerable quantity of dissolved hydrogen, which is not, however, responsible for its brittle nature.

An Improved Form of Crook's Elutriator, by F. J. FRASER.

A new form of this apparatus, possessing advantages over the earlier one, was described.

ROYAL SOCIETY OF ARTS.

The Council have awarded the Society's Silver Medals to the authors of the following papers read before the Society during the past Session:—

Papers read at the Ordinary Meetings:

SIR FRANK BAINES, C.V.O., C.B.E., *The Preservation of Ancient Monuments and Buildings.*

SIR RICHARD A. S. PAGET, BT., *The History, Development and Commercial Uses of Fused Silica.*

MAJOR-GEN. SIR FABIAN WARE, K.C.B.O., C.B., *Building and Decoration of the War Cemeteries.*

FRANK HOPE-JONES, M.I.E.E., *The Free Pendulum.*

BRIG.-GEN. SIR HENRY MAYBURY, K.C.M.G., C.B., *The Victoria Dock District and its Roads.*

T. THORNE BAKER, *Photography in Industry, Science, and Medicine.*

MRS. ARTHUR MCGRATH (ROSITA FORBES). *The Position of the Arabs in Art and Literature.*

Papers read in the Indian Section:

BRIG.-GEN. H. A. YOUNG, C.I.E., C.B.E., late R.A., *The Indian Ordnance Factories and Indian Industries.*

CHEMICAL SOCIETY OF JAPAN.

Papers communicated:—

Studies in Overvoltages. Part III.: Relation of Overvoltage with Surface Tension and Concentration of the Solution, by TADASHI ONODA.

The Quantities of Helium and other
SIR RICHARD M. DANE, K.C.I.E., *Manufacture of Salt in India.*

Papers read in the Dominions and Colonies Section:

C. GILBERT CULLIS, D.Sc., M.I.M.M., *A Sketch of the Geology and Mineral Resources of Cyprus.*

THE RIGHT HON. SIR FREDERICK LUGARD, G.C.M.G., C.B., D.S.O., D.C.L., LL.D., *The Mandate System and the British Mandates.*

Gases contained in Japanese Natural Gases. Part II., by NOBUO YAMADA.

Micro-Determination of Halogens by the Baubigny and Chavanne Method, by HIROSHI NOMURA and JUNKICHI MURAI.

NOTICES OF BOOKS.

A School Chemistry, by O. J. FLECKER, B.Sc. Pp. VIII. + 238. Oxford: The Clarendon Press. 1924. 3s. 6d. net.

Whilst of considerable utility to lecturers and demonstrators, this school chemistry is hardly suitable for pupils in its present form.

It contains much valuable information, and the experiments cover a wide range. Students who have completed the course indicated, should have a good knowledge of practical and theoretical chemistry. Some chapters, *e.g.*, that on "Flame," are very good, and most have been well-chosen. There is a good index, and also a table of logarithms.

At the same time, some of the diagrams are poor. The pneumatic trough is represented as a box, and clamp-stands have been omitted. But most serious of all is the diagram of an apparatus for the determination of equivalent weights, in which a delivery tube is shown as though it passed through the side of the trough.

These defects, unfortunately, detract from the value of such a book, which admittedly contains a good set of experiments.

Nevertheless, science masters and lecturers will undoubtedly find much useful information in the volume. J.G.F.D.

Chemisches Worterbuch (*Chemical Dictionary*), by DR. H. REMY. Pp. VII. + 416. Leipzig and Berlin: Verlag B. G. Teubner. 1924. 10.60 Marks.

This dictionary in the series issued by Teubner, is full of condensed information on general, academic and technical chemistry. It is thoroughly up-to-date, and by close printing and abbreviations (a key to these is furnished) it has been possible to include practically everything of importance in a volume of convenient size.

There are few illustrations, but five valuable tables of the elements and radio-elements are appended.

The Synthetic Dyestuffs and The Intermediate Products, by JOHN CANNELL CAIN, D.Sc., and JOCELYN FIELD THORPE, D.Sc. Sixth Edition. Pp. XV. + 428. London: Messrs. Charles Griffin & Co., Ltd., Exeter Street, Strand, W.C.2. 1923. 21s. net.

The latest edition of this work is divided into three parts. The first part is theoretical, and contains a systematic account of the intermediate products and dyes, commencing with a short chapter on coal tar and its component fractions. Two chapters are given to nitration and sulphonation, and are followed by a description of the amido- and hydroxy-compounds and the acids to be obtained by further treatment. The rest of this section is devoted to the properties and constitution of the various groups of dyes.

Part II. is experimental, and deals in detail with the preparation of dyestuffs and their intermediates. Part III. is concerned with the analysis, valuation and identification of these compounds, including the methods adopted for detecting the dyestuffs on the fabric.

Some of the matter in the theoretical part is of little more than historical interest, and the authors (one of whom, unfortunately, has since died) have evidently found it difficult to keep pace with the rapid technical advances in the subject.

This book is the standard work on the subject, not only for the use of students, but is also frequently consulted by works and dyestuff chemists.

The book is well printed, well arranged, and has a good index.

BOOKS RECEIVED.

Applied Chemistry, by IRA D. GARARD, PH.D. Pp. VI. + 496. 1924. The Macmillan Company, St. Martin Street, W.2. 15s. net.

Examples in Chemistry, by WILLIAM W. MIDDLETON, D.Sc. (Belfast). Pp. VIII. + 134. 1924. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C.2. 3s.

The Scientific and other Papers of Rai Chunital Bose Bahadu, Etc., by J. P. BOSE, M.B., F.C.S. Pp. XXIII. + 523. Vol 1. 1924. Rs. 5.

Airs (For the Hautbois and other Instruments), by E. N. DA C. ANDRADE. Pp. VIII. + 68. 1924. Cecil Palmer, 49, Chandos Street, W.C.2. 3s. 6d. net.

New Patents.

THIS list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

Latest Patent Applications.

14219—Bolton, C. A.—Absorption of sulphur dioxide and hydrogen sulphide. June 12.

14077—Carbide & Carbon Chemicals Corporation.—Processes of making alkyl chlorides. June 10.

14458—Liebknecht, O.—Manufacture of hydrocyanic acid. June 14.

Specifications Published this Week.

194289—Harnist, C.—Manufacture of disinfecting fertilisers from sulphur or metallic sulphides.

216580—American Smelting & Refining Co.—Process for extracting tin from its ores.

216695—Ashcroft, E. A.—Treatment of zinc lead sulphide ores, mattes and the like.

208114—Michael & Co., J.—Processes for making nitrate of potassium.

Abstract Published this Week.

214836—Aryl-phosphinous acids.—Cassella & Co., Ges. L., Frankfurt-on-Main, Germany.

p-Dialkylaminoarylphosphinous acids are prepared by action of phosphorus trichloride upon excess of the dialkylarylamines; a diluting agent such as benzene may be present; the phosphenyl chlorides so produced are then hydrolysed to the corresponding acids or salts, for instance, by means of caustic soda. Substitution products of the dialkylarylamines may be used, particularly meta-substituted derivatives. Examples are given of the production of phosphenyl chlorides, and acids in the form of salts, from dimethylaniline, and dimethyl- or diethyl-*m*-toluidine; sodium, potassium, calcium, copper, iron, and lead salts are described. Other dialkylamines which may be used are 3-chlor-dimethylaniline, 3-alkyloxy-dimethylaniline and tetramethyl-*m*-phenylenediamine. The products are of therapeutic value.

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THE CHEMICAL NEWS,

VOL. CXXIX. No. 3353.

THE SOLID HYDRIDE OF ARSENIC.

By E. J. Weeks, M.Sc., Ph.D., A.I.C., and J. G. F. Druce, M.Sc. (Lond.), R.Nat.Dr. (Prague).

The solid arsenic hydride, AsH, or more probably As_2H_2, was first shown to exist by J. V. Janowsky in 1874 (*Ber.*, 1874, VI., 216). This author obtained it by decomposing sodium arsenide with acids, and ascribed to it the formula AsH.

In 1911, H. Reckleben and J. Scheiber (*Zeitschr. anorg. Chem.*, 1911, LXX., 255) found that the effect of an electric discharge on arsine gave the solid hydride, and they also confirmed the work of Janowsky, except that they assigned to it the double formula, As_2H_2.

Reckleben and Scheiber also showed that if arsine is passed over solid sodium hydroxide and then water, a mixture of arsenic and the solid hydride resulted, in accordance with the equations:

$$AsH_3 + 3NaOH = Na_3As + 3H_2O.$$
$$2Na_3As + 6H_2O = As_2H_2 + 6NaOH + 2H_2.$$

In 1920, H. Thoms and L. Hess (*Ber. Deut. Pharm. Ges.*, 1920, XXX., 483) confirmed the existence of the solid hydride of arsenic which they obtained by the action of water on calcium arsenide.

An account has already been given (Weeks, *The Chemical News*, 1924, CXXVIII., 54) of an attempt to obtain solid arsine by the electrolysis of sodium hydroxide, using an arsenic cathode. The cathode was suspended in a porous pot, the electrolyte being a normal solution of the alkali. A platinum anode was employed. A current of 100 milliamps/cm.^{2} was passed for about half-an-hour. Gaseous arsine was evolved, and a brown deposit appeared in the porous cell. This precipitate was filtered off, washed and dried.

On examination it proved to contain arsenic and hydrogen only.

A similar substance, having the same appearance and apparently identical with the product obtained electrolytically has been obtained by the action of an ethereal solution of stannous chloride upon a solution of arsenic trichloride in aqueous hydrochloric acid. (This substance had been prepared by one of us seven years ago, when a preliminary examination of the body showed that it contained about 98-99 per cent. arsenic and a little hydrogen, but not a trace of tin.)

The reaction, which appears to take place according to the equation:—

$$2AsCl_3 + 4SnCl_2 + 2HCl = As_2H_2 + 4SnCl_4,$$

also occurs in aqueous solution, but not nearly so well or so completely as in ether, in which solvent the yield is about 93 per cent. of the theoretical.

Other solvents for the stannous chloride were tried. Very small amounts of the hydride were obtained, using alcohol, benzene or chloroform.

That the products obtained by the electrolytic and the precipitation methods were identical was established by an examination of their properties. They were quite indistinguishable under the microscope; both were practically insoluble in water and organic solvents. They were insoluble in acids, except in cold or hot concentrated nitric acid (or the hot dilute acid), giving arsenic acid. Aqua regia also disolved both samples. The compound, prepared by either metsod, contains its elements in the proportion demanded by the formula As_2H_2.

Solid arsenic hydride is a brown amorprous substance, stable in air at ordinary temperatures, but readily oxidised when heated. It therefore cannot be dried in a steam oven. It was best obtained in a pure state by washing first with water and then with dilute alcohol, and finally with ether. The washed product was dried in a vacuum desiccator over sulphuric acid. It was only very slightly soluble in water. Deteruinations of solubility were made in the following manner. After stirring a little of the solid with 1000 cc. of conductivity water in a thermostat for half an hour at 20° C. with an electric stirrer, the undissolved solid was filtered off, and the water removed by slow evaporation. In this way it was found that 0.35 gr. of solid arsenic hydride were dissolved by one litre of water.

When examined under the microscope with oblique illumination, using a 2/3 inch Zeiss objective, the substance had an appearance recalling the photographs of the

moon or that of a piece of coke. No crystals were observed.

For the estimation of the arsenic, a weighed quantity of the hydride was dissolved in concentrated nitric acid, and the arsenic was precipitated as magnesium ammonium arsenate, which was ignited to magnesium pyro-arsenate and weighed as such.

0.510 gr. As_2H_2 *gave 1.0350 gr.* $Mg_2As_2O_7$: As = 98.0 per cent. As_2H_2 requires As 98.7 per cent.

Owing to the very small percentage of hydrogen in the compound, combustions of the substance have not given very exact results. Another difficulty also arose during the ignition of the arsine, namely, the tendency of the arsenious oxide formed to volatilise. This compound was, however, retained by the long layer of copper oxide employed, in part at least as a bright green compound, which was formed at the beginning of the copper oxide layer and extended for not more than two inches along the tube. A steady stream of oxygen was maintained during the combustion, which lasted from three to five hours, although it was probably complete after the first half-an-hour. The three experiments gave the following results:—

0.6044 gr. hydride gave 0.1140 gr. water; H = 2.08.
0.6091 gr. hydride gave 0.0657 gr. water; H = 1.20.
0.6987 gr. hydride gave 0.0901 gr. water; H = 1.42.

As_2H_2 requires H = 1.32 per cent.

The green compound formed during the combustion (together with the copper oxide admixed, which could not be removed) was boiled with excess of dilute sodium hydroxide solution and filtered. The filtrate, which was a pale blue colour, was treated with hydrogen sulphide (to precipitate the dissolved copper), and the filtrate from this was acidified with dilute hydrochloric acid, when a yellow precipitate separated. This completely redissolved in sodium hydroxide, so that it was arsenious sulphide, As_2S_3. It thus appeared that the green compound was copper arsenite.

Attempts to prepare similar solid hydrides of antimony and bismuth from the chlorides of the metals by reduction with ethereal stannous chloride were unsuccessful.

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THE CAUSE OF THE COLOUR PRODUCED IN GLASSES OF ANHYDROUS BORAX AND SODIUM METAPHOSPHATE BY FUSION WITH METALLIC OXIDES.

By Theodore Cohn, A.R.C.S., B.Sc.

The fact that many metallic oxides dissolve in fused borax, giving characteristically coloured glasses, has long been known and is extensively made use of in qualitative analysis for the detection of small amounts of copper, cobalt, chromium, iron, nickel and manganese.

J. Donau (*Monatshefte*, 1904, XXV., 913) had shown that in the case of the colour produced in borax beads by small amounts of gold, silver and platinum salts, the colour was probably colloidal in origin. He investigated the question thoroughly in the case of sodium metaphosphate beads, coloured by salts of gold, silver, platinum and the other platinum metals (*Koll. Zeit.*, 1908, II., 273), and proved that the colour was due to a dispersion of the metal itself in the bead in the colloid state, and could be varied by changes of concentration and by varying the heat treatment of the bead. On prolonged heating, the colour gradually passed from red to blue, till finally the metal was completely precipitated, and the bead became colourless. It was also suggested that the colour produced in borax and sodium metaphosphate beads by salts of other metals might be colloidal in nature. A number of experiments were carried out to test the validity of this suggestion.

The tests were carried out on small quantities of borax and microcosmic salt, fused to a bead in a small loop of platinum wire.*

* *This method is disadvantageous for tests carried out in the reducing flame; as the platinum is disintegrated owing to the formation of a brittle carbide. In the case of the Sodium Metaphosphate beads, the disintegration is considerably greater owing to the formation of a platinum phosphide. (W. Heraeus, Zeit. f. Angew, Ch., 1902, XV., 917). Other metals are, however, even more attacked under similar conditions. An attempt to employ small loops of hard glass was unsuccessful, and consequently the platinum loop was used, the period of exposure to the reducing flame being kept as low as possible.*

The oxides of the metals under investigation were used, and the colour of the beads was observed in daylight against a glazed white tile.

The effect of varying the concentration of the metallic oxide in the bead was first investigated. The results are shown in the following table:

CHANGE OF COLOUR WITH INCREASING CONCENTRATION OF THE METALLIC OXIDE.

Oxide.	Sodium Metaphosphate Bead.				Borax Bead.			
	Oxidising flame.		Reducing flame.		Oxidising flame.		Reducing fl	
	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	(
Cobalt.	Light blue →Dark blue.	Bluish-rose →Light purple →Blue.	Indefinite beads. Broadly same as in oxidising flame.		Light blue →Dark blue.		Light blue →Dark blue	
Nickel.	Light brown Orange → →Orange and opaque.	Light greenish brown →Brown →Brown and opaque.	Indefinite beads. Grey and opaque.		Violet-brown → Opaque.	Grey-brown → Opaque.	Grey and opaque.	
Copper.	Light green Dark → green	Greenish blue	Colourless →Red	Colourless →Carmine →Red and opaque.	Light green →Dark green.	Greenish blue.	Colourless →Red.	Red a opaque

It will be seen from the above table that, in general, an increase in the concentration of the metallic oxide causes the colour of the beads to become darker, and finally opaque; there is, however, no actual colour change such as was observed by J. Donau (*loc. cit.*) for gold, silver and the platinum metals.

The only two exceptions to this general rule appear to be:—

(1) The sodium metaphosphate beads with cobalt, in which there is a fairly well-marked transition from the rose beads with very small concentrations of cobalt to the blue beads obtained with greater concentrations. This colour change, however, is a phenomenon often observed in cobalt compounds, and is generally ascribed to the formation of complexes and to intramolecular rearrangements. (Donnan and Basset, *Jour. Chem. Soc.*, 1902, LXXXI., 939). As the colour of the cobalt beads cannot be destroyed by prolonged heating, and in view of the negative results obtained for nickel beads, the colour change cannot be taken to point to the presence of colloid particles in the beads; and

(2) The sodium metaphosphate beads with copper in the reducing flame, in which the change with increasing concentration: Colourless→Carmine→Red→Red and Opaque, does not appear to be quite of the same type as the normal change, because the colourless beads can be obtained with a comparatively large concentration of copper.

The effect of prolonged heat treatment was next investigated. The beads, obtained as already described, were reheated for 30 minutes, and where, on cooling, any indication of a colour change was observed, the heating was continued.

With cobalt, the purple sodium metaphosphate bead obtained in the oxidising flame, gave a blue bead on reheating for 30 minutes and then cooling. Further heating effected no change. The colour change is probably of the same nature as that observed for this bead with increasing concentration of the metallic oxide.

No definite colour changes were observed with beads containing nickel.

With copper, the colour of the red beads obtained in the reducing flame was de-

stroyed by prolonged heating, but only when sufficiently small concentrations of copper were employed. When these colourless beads were treated with water, a red precipitate was formed in the beads after a short time. This shows that the destruction of the red colour on prolonged heating is not a colloidal phenomenon, and points to the formation of a colourless cuprous phosphate.

The final test to be applied was an attempt to precipitate the colloid particles (if any) by the addition of an acid. Sodium metaphosphate beads were worked with, and metaphosphoric acid which is stable at high temperatures was used as the precipitant.

With cobalt and nickel no indications of any precipitation were obtained. Copper in the oxidising flame also gave negative results.

With copper in the reducing flame, however, the addition of metaphosphoric acid caused the red colour of the bead to disappear, as long as the copper content was not excessive, and in this way, colourless beads containing comparatively large amounts of copper were obtained. These beads could be preserved indefinitely in a lightly corked tube, but were decomposed by water, a somewhat coarse red precipitate of copper, which was distinguished from cuprous oxide by the action of concentrated hydrochloric acid, being formed; the bead was thereby rendered opaque. Beads containing somewhat less copper did not lose their transparency entirely, and in these beads it could be seen that the sodium metaphosphate had acquired a light green tinge, indicating the formation of a divalent copper compound.

These facts show that the colourless beads contain a colourless cuprous phosphate, which is decomposed by water into a cupric phosphate and metallic copper, a decomposition exactly analogous to that observed when water reacts with cuprous sulphate (Recoura, *Compt. Rend.*, 1909, CXLVIII., 1105; *Cf.* also V. Auger, *Ibid.*, 1907, CXLIV., 199).

It had now been shown that the colour produced in Borax and Microcosmic salt beads by the oxides of cobalt, nickel and copper was not colloidal in origin, and was therefore due to the formation of coloured metallic borates and phosphates. The nature of these compounds was investigated further.

In the case of borax beads, coloured metallic metaborates are formed; thus with cupric oxide:

$$Na_2B_4O_7 + CuO = Cu(BO_2)_2 + 2\ NaBO_2.$$

No metallic orthoborates are formed, as these are unstable.

In the case of sodium metaphosphate beads, it appears that metallic orthophosphates and pyrophosphates might both be formed:

$$NaPO_3 + CuO = NaCuPO_4;$$
(Orthophosphate.)

$$2\ NaPO_3 + CuO = Na_2CuP_2O_7;$$
(Pyrophosphate.)

and the latter appears from the conditions under which the compounds are formed (*i.e.*, high temperature and an excess of sodium metaphosphate) to be the more probable. It is, however, generally stated that the orthophosphate alone is formed.* To investigate this, the following experiment was carried out:—

A number of sodium metaphosphate beads were heated with cobalt oxide till a clear blue glass was obtained. These coloured beads were powdered, dissolved in dilute nitric acid, and an excess of silver nitrate was added. The liquid was then carefully neutralised by adding dilute ammonia drop by drop. Under these conditions a white precipitate which did not possess the faintest tinge of yellow was thrown down, thus showing that no orthophosphates were present. Similar results were obtained with cupric oxide. When the concentration of the metallic oxide was increased, the same results were obtained as long as the beads formed were transparent; when, however, the concentration of the oxide was so great that solution in the sodium metaphosphate was incomplete,

* *Thus Treadwell states:* (*F. P. Treadwell and W. T. Hall*, ANALYTICAL CHEMISTRY, 5th ed., 1921, Vol. 1, p. 406), "*Just as metaphosphoric acid unites with water on boiling its solution forming orthophosphoric acid,* $HPO_3 + H_2O = H_3PO_4$, *so sodium metaphosphate dissolves, at the fusion temperature, a great many metallic oxides forming characteristically coloured orthophosphates,* $NaPO_3 + CuO = NaCuPO_4$ *(blue bead).*"

the formation of an orthophosphate was indicated by the appearance of a distinct yellow coloration in the precipitate of the silver salt obtained as described above.

CONCLUSION.

The colour imparted to beads of fused borax and sodium metaphosphate by the oxides of cobalt, nickel and copper is not colloidal in nature, but is due to the formation of coloured metallic salts.

With borax beads, metaborates are formed.

With sodium metaphosphate beads, no orthophosphates are produced, as is generally stated, the coloured salts being metallic pyrophosphates.

SUMMARY.

The salts of gold, silver and the platinum metals impart a colour to beads of fused borax and sodium metaphosphate, which is due to the presence of the free metals dispersed throughout the bead in the colloid state. In conformity with the principles of colloid chemistry, the colour of the beads varies with the concentration of the metal and the heat treatment; and the particles can be precipitated by the addition of suitable precipitants (*e.g.*, acids)to the molten beads.

An attempt has been made to produce similar changes in colour, using oxides of cobalt, nickel and copper, but no colour changes of a colloidal nature have been observed. These negative results confirm the view that the colour produced in the beads is due to the formation of coloured metallic borates and phosphates.

In the case of borax beads, metallic metaborates are formed. In the case of sodium metaphosphate beads, the suggestion that only orthophosphates are formed has been investigated. It has been shown, by testing for orthophosphates with silver nitrate, that pyrophosphates alone are produced and no orthophosphates are formed. as long as the beads are transparent.

Colourless heads of sodium metaphosphate have been obtained, containing colourless cuprous phosphate in solid solution. These beads are stable in air, but are decomposed by water with the production of cupric phosphate and metallic copper.

In conclusion, I wish to express my thanks to Professor H. Brereton Baker, F.R.S., for his kind interest in this work.

Imperial College of Science and Technology,
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July 1, 1924.

CHROMIUM DIOXIDE.

BY GEOFFREY N. RIDLEY.

PREPARATION.

Many methods have been devised from time to time for the preparation of chromium dioxide. Some of these processes are very convenient for laboratory practice; others are inconvenient in that they take too long, and the quantity of oxide prepared is often useless.

Wet Methods.

(*a*) Perhaps the commonest method in this category is that devised by Schweiger, which consists in passing nitric oxide into a warm dilute solution of $K_2Cr_2O_7$:

$$2K_2Cr_2O_7 + 2NO = 2KNO_3 + K_2CrO_4 + 3CrO_2.$$

The precipitate is washed with water and alcohol and dried at 258° C.

A great deal of time is required for the satisfactory precipitation of CrO_2 in this process, and good results are largely dependant upon the conditions to which the dichromate is subjected while in solution.

(*b*) Potassium dichromate may also be reduced by $Na_2S_2O_3$, with similar results.

(*c*) Chromium dioxide is produced when K_2CrO_4 is treated with a conc. solution of $Cr_2(SO_4)_3$ or $CrCl_3$:

$$5K_2CrO_4 + Cr_2(SO_4)_3 = 3K_2SO_4 + 2K_2Cr_2O_7 + 3CrO_2.$$

(d) An additional method may be inserted here. It depends upon the reduction of chromic acid by stannous chloride.

It is, however, very imperfect, and the desired reaction may not take place unless various uncertain physical conditions are adhered to. A study of these conditions may form the basis of subsequent investigations.

The following equation illustrates the probable course of the correct reaction:

$$H_2CrO_4 + 3SnCl_2 = SnCl_4 + 2SnOHCl + CrO_2.$$

(*e*) The action of light upon a strong aqueous solution of CrO_3 also causes the gradual deposit of chromium dioxide.

Dry Methods.

Compared with the wet, the dry methods are more convenient, generally speaking, for the preparation of CrO_2. They do not, as a rule, however, yield the oxide in as

pure a condition as may be desired, but is *liable to be contaminated by other substances* which have to be removed by suitable means. *The dry methods are*, nevertheless, very suitable for the production of chromium dioxide in quantity.

(*a*) Moissan's method is to heat Cr_2O_3 in air or oxygen up to 400° C.

(*b*) Krüger advises the heating of $Cr_2O_3.xH_2O$ in air up to 250° C.

(*c*) CrO_2 is also formed at an intermediate stage in the heating of CrO_3 at 250° C. This procedure is about the most suitable way of preparing the dioxide, since the temperature conditions can be carefully regulated.

Additional methods are:

(*d*) To pass sulphur dioxide over heated CrO_3. Quantities of SO_3 are formed, and a *black or dark grey mass* of CrO_2 is left in the combustion tube:

$$SO_2 + CrO_3 = SO_3 + CrO_2.$$

The solid is removed, and any sesquioxide or trioxide present may be extracted by washing the finely ground substance several times with dilute H_2SO_4.

(*e*) To gently heat a mixture of phosphorus and CrO_3 in a crucible until the whole takes fire. Unless the proportion of phosphorus to oxide is correctly maintained other substances are liable to be formed, including phosphides of chromium.

PROPERTIES AND CONSTITUTION.

With regard to the properties of chromium dioxide, there are several interesting points to be noted. It is a dark grey, almost black, solid. It is insoluble in liquids, such as ether, acetone, etc. When heated to 300° C. it evolves oxygen, being converted into the lower oxide, Cr_2O_3.

When heated in a current of chlorine at about 250° C., it forms a compound—$Cr_3O_6Cl_2$. Treatment with HCl or HCl and H_2SO_4 causes the evolution of chlorine (Moissan). It is unattacked by PCl_5. It reacts quite vigorously with hydrogen peroxide, evolving oxygen very rapidly at 68° C. The addition of a few drops of dilute H_2SO_4 produces the blue colouration of perchromic acid. This furnishes evidence *in favour of the theory that chromium dioxide* is expressed—Cr_2O_3, CrO_3.

When the powdered oxide is boiled for a long time with extremely concentrated sodium hydroxide solution, it breaks up, yielding the hydroxide, $Cr(OH)_3$ and sodium *chromate*.

From the point of view of its constitution, chromium dioxide is looked upon as *chromic chromate*, Cr_2O_3, CrO_3. It is an unfortunate term, since this name hardly agrees, in the strict sense, with the formula assigned to it. The *theoretical* expression would be Cr_2O_3, $3CrO_3$; its reaction with strong alkali would then be represented by the equation:

$$Cr_2(CrO_4)_3 + 6NaOH = 2Cr(OH)_3 + 3Na_2CrO_4.$$

Chromium dioxide appears to embody *both basic and acidic characters*, a feature which is admirably demonstrated by its behaviour with NaOH, mentioned above. Further, it furnishes one of those comparatively rare cases in which an element exists in an apparently double state of valency in combination with other elements. The oxide of lead, Pb_2O_3, is an example, it being expressed correctly thus: PbO. PbO_2.

ERRATA.

A NOTE ON "THE SIGNIFICANCE OF THE ELECTRODE POTENTIAL," BY J. HEYROVSKY.

Vol. CXXVIII., June, 6, p. 359, col. 1, 3rd line: the formula should be

not omit the work term $\frac{RT}{F} \log \epsilon'_m/\epsilon_m$,*

9th line: instead of = should be −, so that the equation is

$$E' - E + \frac{RT}{F} \log \frac{\epsilon'_m}{\epsilon_m} - \phi'_m + \phi_m$$
$$= \pi - \pi' + E_s - E'$$

6th line from below: after K should be −, so that the formula is

$$E = K - \frac{RT}{F} \log p + I - M + \frac{RT}{F} \log \quad C_{MeOH}/C_{OH} - H_{MeOH},$$

harles University of Prague.
une 15, 1924.

STUDIES IN THE REACTIONS OF THE AMINO GROUP IN 4′ AMINO 1 PHENYL 5 METHYLBENZOTHIAZOLE.

Part X.—Azo Dyes from the Sulphonic Acid of Dehydrothiotoluidine and the Bromination of Dehydrothiotoluidine Sulphonate Azo α Naphthol and Dehydrothiotoluidine Sulphonate Azo β Naphthol in Glacial Acetic Acid Solution.

By R. F. Hunter, A.R.C.Sc., M.S.Chim., F.C.S.

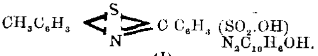
This paper is essentially the continuation of the work in Parts VIII. and IX. of this series of papers, and deals with the azo dyes of dehydrothiotoluidine sulphonic acid and their bromination.

It is well known that the introduction of a sulphonic acid group into a dye intermediate has usually the effect of enriching the colour of the resultant azo derivatives by deepening the shade and promoting greater fastness to light and washing.

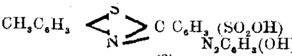
The monosulphonic acid of dehydrothiotoluidine is well known, and was first prepared by Green, by sulphonation of the thiazole in sulphuric acid solution with pyrosulphuric acid at a temperature below 50° C. Green converted the acid into the ammonium salt and analysed the latter. Up to the present there appears to be no means of obtaining the free pure thiazole from its ammonium salt, though if this were possible it would mean that a successful method of preparation of pure dehydrothiotoluidine had at last been found. The sulphonic acid further forms the method of separation of primuline and dehydrothiotoluidine by the Kalle method (Meyer, *loc cit.*).

The formula assigned to the compound is that of dehydrothiotoluidine substituted with a sulphonyl group in the phenylating part of the molecule. The acid is no doubt formed in a manner analogous to the production of sulphanilic acid from aniline, namely, by conversion of the original thiazole into the sulphate and the migration of the sulphonyl group from the amino group. The para position is, of course, blocked in the case of dehydrothiotoluidine by the substituting 5 methyl benzothiazole system. It is clearly necessary to assume migration to another position, therefore. The sulphonic acid used in these experiments was prepared by dissolving dehydrothiotoluidine in pyrosulphuric acid, and keeping the solution at a temperature of 50° C. for some time, drowning the liquid in cold water and filtering off the precipitated sulphate of the base; drying this, and diazotising suitable amounts of this with the theoretical sodium nitrite, and coupling with suitable couplers in the preparation of the thiazole dyestuffs previously discussed in these papers (*loc. cit.*). The four azo compounds prepared were those formed by diazotising dehydrothiotoluidine sulphonic acid with the naphthols, resorcinol and salicylic acid, that is to say, the couplers used were the same as those used in the cases of 4′ amino 1 phenyl 5 methylbenzothiazole and nitrodehydrothiotoluidine, such that the properties of the azo compounds from these three intermediates might be compared under the same conditions of preparation, etc.

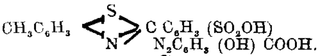
The azo compounds should, of course, be (1), (2) and (3):



(1)



(2)



(3)

The introduction of a sulphonic acid group greatly improves the quality of the azo dyes formed from the thiazole intermediate. The introduction of a sulphonic acid group, however, increases the solubility of the compounds, and it is not therefore recommended to digest the azo dyes with hot water for any length of time to remove the last traces of salt, as was done in the previous cases. The colours are better. The red, particularly that derived from resorcinol, is brighter, and the azo compounds are obtained in a better state than in the case of nitrodehydrothiotoluidine (*loc. cit.*).

As has already been stated, one of the purposes of this series of investigations on 4′ amino 1 phenyl 5 methylbenzothiazole is to provide new thiazoles for the study of bromination of the fused thiazole ring in

benzothiazoles of the type of dehydrothiotoluidine and its homologues, with a view to definitely establishing the hypothesis which has been advanced by the author as regards the bromination of the thiazole ring in benzothiazoles, namely, that bromination and the addition of bromine in solvents such as glacial acetic acid and ethyl alcohol, consists in the normal splitting of the double bond between the nitrogen and carbon atoms of the thiazole nucleus, with *the addition of two atoms of bromine at the* nitrogen and carbon atom respectively (*loc. cit.*), and (Bromination of substasces containing a thiazole ring (this Journal). As has been indicated in past papers on this subject, the addition in the case of dehydrothiotoludine, the dehydrothioxylidines, acetyl dehydrothiotoluidine, and other substituted benzothiazole systems of this type, consists of two bromine atoms, but there is a somewhat peculiar observation on *record as to the formation of brom addition* products in the benzothiazole series, namely, the observation of Bogert and Abrahamson (*Jour. Amer. Chem. Soc.*, 1922, XLIV., 826), that 1 phenyl benzothiazole, the parent substance of the dehydrothiotoluidine derivatives, adds four bromine atoms in glacial acetic acid. The suggestion was put forward by the author that in 1 phenyl benzothiazole, where the homocyclic six-membered ring of the bicyclic *benzothiazole system is unsubstituted*, a para bridge bond may exist in the homocyclic ring joining the carbon atom 5 and the para carbon carrying the fused nuclei by a slanting bridge bond, as would appear to exist in naphthalene, a fused homocyclic bicyclic ring system in some ways analogous to benzothiazole, for the thiazole ring is nothing more than the benzene ring in which three carbon hydrogen groupings have been replaced by a sulphur and nitrogen atom. The bridge bond under the action of bromine in glacial acetic acid solution rupturing to add four atoms of bromine in conjunction with the nitrogen carbon double linkage in the thiazole ring, addition taking place at position 5, which later is substituted by bromine if the solution is warmed, this being in accordance with the rule of addition preceding substitution.

In view, then, of what has been stated above, it was decided to examine the bromination of benzothiazoles substituted by various groups in various positions, with a *view to obtaining some information as to* how the substitution affects the addition of halogen, and two of the azo compounds prepared from the sulphonic acid of dehydrothiotoluidine were therefore dissolved in glacial acetic acid by warming, and brominated in the usual way by adding bromine drop by drop from a burette, when the usual type of products separated. This was, of course, only done on a very small scale, and the quantities of products isolated *much too small or analysis*, or even any real examination. The observation is, however, of interest, and it is hoped to repeat it at a later date on a somewhat larger scale, and analyse the products of the reaction.

It is to be expected, of course, that dehydrothiotoluidine sulphonate azo naphthols will add bromine in the normal way at the double bond of the thiazole ring to give substances of the constitution (4).

$$CH_3C_6H_3 \overset{S}{\underset{NBr}{<\quad>}} CBr\ C_6H_3\ (SO_2OH)\cdot$$
$$N_2C_{10}H_6\ (OH).$$

(4)

It would be interesting to examine the effect of the azo naphthol grouping on the brom thiazole ring, since substitution in the substituting phenyl of the dehydrothiotoluidine system clearly affects the character of the brom thiazole compounds. A familiar example of this is the fact that dehydrothiotoluidine dibromide is a stable substance, while acetyldehydrothiotoluidine dibromide is most unstable where the amino group in the substituting phenyl is acetylated thus, acetyldehydrothiotoluidine dibromide splits off bromine on merely warming with water, while dehydrothiotoluidine dibromide is quite stable to the latter.

Experimental.

Dehydrothiotoluidine:

The industrial intermediate supplied by the B.D.C. was used in these experiments. This, of course, contains something more than a trace of primuline which, however, does not appear to have any deteriorating effect on the character of the resulting azo dyes produced by diazotisation and coupling in the usual manner (*loc. cit.*).

Dehydrothiotoluidine Sulphonate:

15 gms. of dehydrothiotoluidine, in the form of a fine powder, were weighed into an evaporating basin and made into a brown solution with pyrosulphuric acid, and the solution kept at 50° C. for a little over an hour. The resulting brown solution was then drowned in cold water, and the precipitated sulphate filtered and washed at the pump, and finally dried on the steam. This was used for the preparation of the azo dyes.

Dehydrothiotoluidine sulphonate azo resorcinol:

5 gms. of the dry sulphonation product, prepared as above, were dissolved in 30 ccs. of concentrated sulphuric acid, and the solution diluted to 100 ccs. with ice water and small pieces of clean ice. The solution was then cooled to 0° C. in a refezing mixture, and the theoretical nitrite in 30 ccs. of ice water run in with stirring. To the diazonium solution was then added the theoretical resorcinol in 30 ccs. of 2N caustic soda from a tap funnel. The first drop of coupler produced an immediate red precipitate, and this increased with the addition of further coupler. The solution was stirred a few minutes after the completion of the addition, and then allowed to stand for half an hour. Salt was then added, and the mixture allowed to stand while the azo compound separated out. The precipitated azo compound was filtered, washed with water, a little dilute alcohol, and dried. It was then digested with hot water (this is not advisable), filtered, and washed with a little alcohol, and weighed when dry.

Yield, 2 gms.

The azo compound was examined in the usual way.

Examination:

The azo compound is a much brighter red than the azo compound obtained from dehydrothiotoluidine and nitrodehydrothiotoluidine. It dissolves in concentrated sulphuric acid to give a deep red solution.

Dehydrothiotoluidine sulphonate azo α naphthol:

5 gms. of the sulphonation product were dissolved in acid, the solution diluted with ice and ice water to 100 ccs., and cooled in a freezing mixture till the temperature was 0° C., when the necessary sodium nitrite in 30 ccs. of ice water was run in from a tap funnel with stirring. The theoretical naphthol in 30 ccs. of 2N caustic soda previously cooled in ice was then run in from a tap funnel with stirring, the liquid allowed to stand, salt added, allowed to stand, and the precipitated azo compound filtered off, washed and dried. The azo compound was digested with warm water, filtered, and washed with a little ethyl alcohol and dried.

Yield, 3.5 gms.

The azo compound was examined as before.

Examination:

The red azo dye dissolves in concentrated sulphuric acid to give a deep bright blue solution. On drowning this in cold water a red solution and precipitate is again produced. The azo compound is appreciably soluble in hot glacial acetic acid to give a red solution.

Dehydrothiotoluidine sulphonate azo β naphthol:

5 gms. of the crude sulphonated product was dissolved in acid, the solution diluted to 100 ccs. with ice and ice water, the solution or suspension cooled to 0° C. in a freezing mixture when the theoretical sodium nitrite in 30 ccs. of ice water was run in with stirring, the usual precautions being maintained. To the diazonium solution was then added the theoretical naphthol in 30 ccs. of 2N caustic soda, previously cooled in a freezing mixture, from a tap funnel with stirring. The liquid was left for half an hour, salt added, left for another half hour, the precipitated azo compound filtered, washed and dried. The dry azo compound was digested with warm water, filtered, and washed with a little alcohol, dried, and weighed.

Yield, 4 gms.

Examination:

The red azo compound dissolves in concentrated sulphuric acid to give a deep bright violet solution, which, on dilution with cold water gives a red solution. The azo compound is appreciably soluble in hot glacial acetic acid to give a red solution.

Dehydrothiotoluidine sulphonate azo salicyclic acid:

5 gms. of sulphonic acid were dissolved in acid, the solution diluted with ice and ice water and cooled to 0° C., when the theoretical sodium nitrite in 30 ccs. of ice water was run in. To the diazonium solu-

tion was then added the necessary salicyclic acid in 30 ccs. of cooled caustic soda from a tap funnel, the liquid allowed to stand, the azo compound salted out, and washed, dried, digested with hot water, washed with dilute alcohol and weighed after drying.

Yield, 2 gms.

Examination:

This azo compound is brown in colour, and dissolves in concentrated sulphuric acid to give a brown solution.

Bromination of dehydrothiotoluidine sulphonate azo α naphthol:

The bromination was carried out in the usual way. A small quantity of the red azo compound was dissolved in glacial acetic acid to a red solution, and the solution cooled somewhat.

To the solution was then added bromine, drop bp drop from a burette charged with the latter. The liquid turned a deeper red, and then a brown colour, with the separation of a fine precipitate. Drowning the mixture in water completed the precipitation. The yield was too small for investigation.

Bromination of dehydrothiotoluidine sulphonate azo β naphthol:

As before, a small quantity of the red azo derivative was dissolved in glacial acetic acid by warming to a red solution. This was cooled somewhat and bromine added drop by drop, when the solution darkened in colour and then turned a brown colour with the separation of a fine precipitate. Drowning in cold water completed the precipitation. Here, again, the yield was too small for investigation.

The introduction of a sulphonic acid into the molecule of 4′ amino 1 phenyl 5 methylbenzothiazole appears to improve its qualities as an azo dye intermediate.

The azo dyes formed by diazotising the sulphonic acid and coupling with the naphthols were dissolved in glacial acetic acid and brominated, when brown-red precipitates made their appearance.

Highbury New Park, N.5.

April, 1924.

GENERAL NOTES.

CANADIAN DIATOMACEOUS EARTH

Owing to the greatly increased use of diatomaceous earth, the Mines Branch of the Department of Mines, Ottawa, is now investigating the Canadian sources of supply.

Trade names for the material are: Diatomaceous earth, kieselguhr, tripolite, tripoli, and infusorial earth. The last is erroneous, and tripoli is usually understood to denote material used for the same purposes, but of a different origin. The dry earth, when pure, is an extremely light, chalky looking porous substance, composed of microscopic siliceous skeleton diatoms formed by the agency of aquatic plants. Over 5,000 different varieties of these diatoms, which present beautiful shell-like structures under the microscope, have been described. It is not plastic, and between the teeth is not gritty, but sponge-like. There are upwards of a hundred uses for diatomaceous earth. Some of these are for polishes and cleansers; filters; insulators against heat, cold and sound; as fillers for any material that requires maximum bulk with minimum weight; for fireproofing and packing materials; in the manufacture of water glass, etc., etc. The size and structure of the diatoms and the relative purity of the material play an important role in its ultimate uses.

The earth occurs in Canada, in beds of varying thickness on the bottoms of existing and ancient lakes in the Maritime Provinces and British Columbia. Nearly one hundred occurrences are now known in Nova Scotia and south-eastern New Brunswick, mostly in the northern part of Nova Scotia. The best grades are usually found on the higher lands, near the sources of streams and rivers, or where the deposits have not been contaminated or disturbed by spring freshets. All the eastern occurrences are in lakes or bogs. The wet earth is rarely snow white, but is grey or pale brown in colour, usually, however, drying white. There are certain deposits that are overlain by a peaty substance, which, when dry, readily ignites and smoulders away, leaving a white fluffy ash which is a good grade of diatomaceous earth. A large deposit at Digby Neck, on the west coast of Nova Scotia, is a good example of this class of material. Most of the eastern deposits

are less than four feet deep of commercially pure earth and of small extent, and some are far from a railway. There are at least half a dozen, however, that are large and pure enough for economic working. The Oxford Tripoli Company, whose deposit is at Silica Lake in Colchester County, N.S., is the only firm in the Dominion at present engaged in producing this material.

In British Columbia there are about twenty known occurrences of diatomaceous earth, but with the exception of the Quesnel deposits, none are of commercial importance under present conditions. Unlike the eastern deposits, those of British Columbia are mostly dry and compact. Quesnel, on the Fraser River, is the present terminus of the Pacific Great Eastern Railway between Vancouver and Prince George, and the beds there are by far the largest and purest known in the Dominion. There are a dozen or more exposures over an area of 30 to 40 square miles, and some of the beds are 40 feet thick and from 600 to 800 feet above the present river. They stand out as white bluffs on the steep banks, or have been exposed by landslides and are visible for miles. Many of the deposits are dense and hard, so that the earth could be cut into blocks for filters or other purposes. The country round Quesnel is both interesting and picturesque, for besides these remarkable white beds, beautiful coloured clays are exposed and often stand out as weirdly shaped pinnacles and turrets a hundred feet or more high. These clays include deposits of china clay and material suitable for pigments and moulding. At present no use is being made of these valuable materials, but now that the railway is at Quesnel, their development should not be long delayed.

For marketing, the earth is first dried. either in the open air, or in revolving kilns, and then roasted to burn off the carbonaceous matter (a process called calcining), after which it is graded, first by screening into different sizes, and then by a system of settling in a current of air The extent and nature of the treatments depends on the different uses for which the product is required.

The earth from the eastern deposits would have to be calcined for most uses. but that at Quesnel could be utilised for many purposes after only preliminary drying.

Owing to the numerous and varied uses of diatomaceous earth, statistics as to the actual quantity consumed in different trades in Canada are at present unobtainable, but it is known to be large and practically all of it is imported.

The United States production is roughly 100,000 tons annually, fifteen per cent. of which sells at $100 or more per ton, the price of the crude averaging $15, and ordinary grades $30.

It would seem, therefore, that more general interest and appreciation of this useful material might lead to a considerable increase in the home consumption and exportation of the Canadian diatomaceous earths.

DYESTUFFS (IMPORT REGULATION) ACT, 1920.

APPLICATIONS FOR LICENCES IN JUNE, 1924.

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during June, has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee:—

The total number of applications received during the month was 411, of which 316 were from merchants or importers. To these should be added 9 cases outstanding on June 2, making a total for the month of 420. These were dealt with as follows:

Granted—296 (of which 278 were dealt with within 7 days of receipt).

Referred to British makers of similar products—65 (of which 54 were dealt with within 7 days of receipt).

Referred to Reparation Supplies available—24 (all dealt with within two days of receipt).

Outstanding on June 30, 1924—35.

Of the total of 420 applications received, 356, or 85 per cent., were dealt with within 7 days of receipt.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE FARADAY SOCIETY.

JULY 7, 1924.

The Electrolysis of Solutions of Potassium Oxalate with a Tin Anode, and an Electrometric Determination of the Constitu-

tion of the Complex Anions Formed, by F. H. JEFFERY, M.A.

The following experiments were made to examine *the passage of electricity during* electrolysis from a tin anode to aqueous solutions of potassium oxalate.

Hausmann and Löwenthal prepared crystals which they regarded as $K_2C_2O_4.SnC_2O_4.H_2O$. Rosenheim and Max Platsch obtained a substance which they represented by the formula,

$$\begin{array}{ll} CO \, . \, OSn & (CO \, . \, O{-}CO{:}OK)_3 \\ | & \qquad\qquad + 5H_2O \\ CO \, . \, OSn & (CO \, . \, O{-}CO{:}OK)_3 \end{array}$$

For preliminary experiments to find whether kations were formed in sufficient concentration to give a deposit on the kathode, the tin anode was placed inside a porous pot containing potassium oxalate, this pot was surrounded by a solution of oxalic acid of the same gram equivalent concentration as that of the anolyte, and in this was placed the platinum kathode.

Experiments to obtain solids derived from the tin anode often lasted during five or six days; for these the platinum kathode was placed in a porous pot containing a concentrated solution of ammonium oxalate; this porous pot was placed inside a much larger porous pot containing potassium oxalate solution of the same concentration as that used for the anolyte which surrounded this outer pot.

For currents of 0.4 to 0.01 amp. no tin was found on the kathode nor in the katholyte; the tin went into solution entirely as complex anions.

For all current densities used the anion formed during several hours from the beginning of an electrolysis was derived from divalent tin. No gas was evolved from the anode at this stage.

After a time there was a sudden drop in the current and a rapid rise in the potential from anode to cathode.

At this stage the anode was coated with a fine deposit of black metal.

If the electrolysis was continued without removing this deposit, oxygen was evolved at the anode. In a typical experiment with a twice normal oxalate solution and a current of 0.05 amp., the area of the anode being 12 × 12 $cms.^2$ the evolution of oxygen was 31 cc. per amp. hour.

If the electrolysis was continued further, it was possible to oxidise completely the compound in solution and also crystals derived from divalent tin to compounds derived from tetravalent tin.

At an intermediate stage tin continued to go into solution from the anode as a stannous complex concomitantly with the oxidation; the anode was coated with white crystals of stannous material above the black finely divided metal, the anolyte containing principally the stannic complex in solution.

Provided crystals on the anode were removed from time to time, it was possible to maintain the current constant for hours during the oxidation, but a low current density was necessary.

Alike during the formation of the stannous complex and of the stannic complex the anolyte became acid.

At the conclusion of an electrolysis in which oxidation had continued for many hours, the voltage from anode to cathode immediately after switching off the current was high; it was 3.2 volts for normal solutions, rising to 3.4 volts for thrice normal solutions.

During these oxidations no tin was deposited on the kathode: complex anions alone were formed.

Each measurement was made by first finding the electromotive force of the system:—

$$Hg \mid Hg_2Cl_2, \text{ satd. } KCl \parallel \text{satd. } KCl \parallel \text{anolyte} \mid Sn$$

and then immediately finding the electromotive force of the system—

$$Hg \mid Hg_2Cl_2, \text{ satd. } KCl \parallel \text{satd. } KCl \parallel Hg_2Cl_2, \text{ n}KCl \mid Hg.$$

The anolyte consisted of 200 cc. of potassium oxalate solution approximately twice weight normal saturated with the potassium salt of the stanno-complex, crystals of the latter being present on the bottom of the dish containing the anolyte. The anolyte and crystals were stirred vigorously during all measurements. Before each measurement the tin anode was cleaned by gently rubbing it with fine emery paper and washing with distilled water.

From these experiments it appears that electricity passes from anode to anolyte in accord with the equation—

$$Sn + 2C_2O_4'' - 2 \ominus = [Sn(C_2O_4)_2]'',$$

electrometric determinations having shown that the stanno-complex anion is of the form $[Sn(C_2O_4)_2]''$.

A solid phase corresponding with this complex ion,

$K_2[Sn(C_2O_4)_2].H_2O$,
can be isolated.

When the tin anode is coated with finely divided metal and the products of electrolysis allowed to accumulate on it, anodic oxidation takes place probably in accord with the equation—

$[Sn(C_2O_4)_2]'' + C_2O_4'' - 2 — = [Sn(C_2O_4)_2]''$,

concomitantly with this there is an evolution of oxygen even with very small anodic current densities—

$2OH' - 2 — = H_2O + 1/2O_2$.

A solid phase derived from tetravalent tin is formed, but it has not been determined whether it is of the form,

$Sn(C_2O_4)_2$ or $K_2[Sn(C_2O_4)_3]$.

No tin is deposited on the kathode during this stage.

The generalisation of Meyer-Jacobson (1913) does not appear to be consistent with the results of these experiments, nor does it appear that the chemical individual postulated by Rosenheim (1899) has been produced during these electrolyses.

The anode potential remains constant for a wide range of current density provided the anode be kept free from finely divided metal and the products of the electrolysis: failing this precaution it may rise to over nine volts, referred to the normal hydrogen electrode as zero, the current being 0.1 amp.

The Darwin Thread. Recorder has been adapted to measuring variations of the electrolysis current and also the time-integral of this current. It shows the rapidity of the change from the stage of the formation of the stanno complex alone to the stage of anodic oxidation.

PHYSICAL SOCIETY OF LONDON.

A Special Meeting of the Society will be held at Cambridge, on Saturday, July 19, 1924, by kind invitation of Sir Ernest Rutherford and of the Directors of the Cambridge and Paul Instrument Company.

Dr. G. F. C. Searle will exhibit and demonstrate some new class experiments.

The following communications will be given at the Cavendish Laboratory:—

Radiations in a Discharge Tube, by Sir J. J. Thomson, O.M., F.R.S.

Recent Experiments on the Artificial Disintegration of the Elements, by Sir Ernest Rutherford, F.R.S., and Dr. J. Chadwick.

A Two-Dimensional Recording Accelerometer for Aeroplane Research, by Dr. G. F. C. Searle, F.R.S.

Proceedings at the meeting on June 27, F. E. Smith, C.B.E., F.R.S., in the chair:

Thermionic Emission from Systems with Multiple Thresholds, by Prof. O. W. Richardson, D.Sc., F.R.S.

In the introductory part of this paper, reasons are given why it is necessary at the present time to face the question of the connection between thermionic emission and the internal electron levels of the emitting substance. The theoretical problem is attacked from three different points of view, namely, (*a*) classical statistical mechanics, (*b*) chemical dynamics, and (*c*) the laws of photo-electric action. As a result of this discussion it seems possible to exclude certain alternatives which might otherwise have appeared not improbable and to formulate a set of rules governing the fundamental phenomena which are not in conflict either with the known facts or with any well-recognised relevant principle.

A Demonstration of *A Selenium Photometer* was given by Dr. F. C. Toy.

This instrument was designed for use by photographic manufacturers in measuring the density of a negative after test exposures which vary from strip to strip of the negative. The intensities of two beams of light are compared, one of which passes through the part of the negative to be tested, while the other passes through a compensating wedge which has to be adjusted until its effect on the second beam is equal to that of the negative on the first beam. A singl lamp is employed, the light from which falls on two circular opals, each about 5 mm. in diameter, which are arranged on opposite sides of the lamp and serve as the sources of the two beams. The latter are deflected by means of prisms, one passing through the negative while the other passes through the compensating wedge; both eventually fall on a selenium cell in the circuit of which is a sensitive ganvanometer. Two shutters, one for each beam, are mounted at opposite ends of a pivoted arm and are so designed that as one beam is progressively obscured by one shutter, the other beam is progressively opened by the other, the total illumination of the selenium cell remaining constant, provided that the two beams on reaching it are of equal intensity. The wedge is there-

fore adjusted until, with the required negative in position, there is no change in the deflection of the galvanometer on turning the shutter. The method is extremely accurate. If the opacity of the negative be 10, cutting the light-intensity down to 1/10th of its value so that the density, or logarithm of the opacity, is 1, extreme readings differ by 0.002 per cent. For a density of 5 the difference is less than 0.01 per cent.

A Method of Measuring very Small Capacities, by L. HARTSHORN, A.R.C.S., B.Sc., D.I.C.

A Demonstration of *A New Form of String Galvanometer* was given by PROF. ERNEST WILSON.

A Demonstration of *The Phosphorescence of Fused Transparent Silica* was given by DR. W. E. CURTIS, King's College.

The phenomenon, to which attention has been called by various observers, was demonstrated, using a mercury lamp and a hydrogen tube, both of transparent silica. The effect of heat in increasing the intensity of the phosphorescence and decreasing its duration was also shown.

Observations made on a silica tube containing helium and a very slight trace of hydrogen were described. It was found that whereas a condensed (oscillatory) discharge gave the Balmer lines faintly and feeble phosphorescence, an uncondensed (unidirectional) discharge developed neither Balmer lines nor phosphorescence. There was also a correspondence between the localisation of the Balmer lines and that of the phosphorescence. On admitting hydrogen to the helium tube by heating it red hot in a blowpipe flame, the phosphorescence was obtained strongly. These observations suggested that the effect might be due to radiation of wavelengths occurring in the hydrogen spectrum, but absent from the helium spectrum, and it was pointed out that the Lyman series of hydrogen, which lies between $\lambda\lambda$ 1,215-912 A, was probably the effective radiation, since there are in this region no helium lines. Some support is lent to this view by the fact of the strong absorption of quartz in the region in question, the centre of its absorption band being situated at about λ 1,050 A. The other gases whose radiations are effective in producing phosphorescence are also believed to give rise to lines in this region.

THE GEOLOGICAL SOCIETY.

JUNE 25, 1924, DR. J. W. EVANS, C.B.E., F.R.S., PRESIDENT, IN THE CHAIR.

Communication read:—

The River-Deposits of the Lower Valley of the Warwickshire Avon, by MISS MABEL ELIZABETH TOMLINSON, B.A., M.Sc., F.G.S.; with an Appendix by Alfred Santer Kennard, A.L.S., F.G.S., and Bernard Barham Woodward, F.L.S., F.G.S.

NOTICES OF BOOKS.

A Textbook of Inorganic Chemistry, Edited by J. NEWTON FRIEND, D.Sc., PH.D., F.I.C. Vol. 2: *The Alkali Metals and their Congeners*, by A. JAMIESON WALKER, PH.D., B.A., F.I.C. Pp. XXVI. + 379. London: C. Griffin & Co., Ltd., Exeter Street, Strand. 1924. Price 20s.

Volume 2 of Dr. Friend's *Textbook of Inorganic Chemistry* is devoted to the alkali metals and their congeners, and has been written by Prof. Walker.

The occurrence, history, preparation, properties (chemical and physical), atomic weight determinations, compounds, detection and estimation of each of the elements (and the radicle NH_4) are described in order. The latest information has been included, and there are extensive references at the foot of practically every page. These, it is stated, have been checked by Mr. F. W. Clifford, librarian of the Chemical Society, and his assistants.

Hydrogen has been included in Group 1 of the Periodic Classification. The inclusion of this element has been the subject of much controversy since Mendeléef first proposed it in 1872. Reasons for placing it at the head of the halogen group have been suggested from time to time. Most of these, however, are simply arguments against its inclusion in Group 1, with the elements of which it certainly has decided resemblances. Loring has recently published in this Journal a Wedge Periodic Scheme, in which its relationship to the alkali metals is indicated without it being actually incorporated in this group.

It is to be hoped that the remaining volumes of the series will appear without undue delay, so that chemists may be able to refer to reliable information over the whole range of inorganic chemistry.

The attention of librarians may be directed to the reasonable price asked by the publishers for such a comprehensive work. T.G.F.D.

BOOKS RECEIVED.

Matter and Change—An Introduction to Physical and Chemical Science, by WILLIAM CECIL DAMPIER WHETHAM, M.A., F.R.S. Pp. VI. + 280. 1924. The University Press, Cambridge.

The U.S. Department of Commerce, Bureau of Standards, has issued the following bulletins:—

Some Methods of Testing Radio Receiving Sets, by J. L. PRESTON and L. C. F. HORLE. Pp. 203 to 228.

Emissive Tests of Paints for Decreasing or Increasing Heat Radiation from Surfaces, by W. W. COBLENTZ and C. W. HUGHES. Pp. 171 to 187.

A Camera for Studying Projectiles in Flight, by H. L. CURTIS, W. H. WADLEIGH and A. H. SELLMAN. Pp. 189 to 202.

United States Government Master Specification for Coal Tar Pitch for Waterproofing and Damp Proofing. Pp. 2 to 11.

Mr. F. S. Spiers, Secretary and Editor to the Faraday Society, and Secretary to the Institute of Physics, has moved his office to 90, Great Russell Street, W.C.1 (Telephone, Museum 5718). The Publishing Office of the *Journal of Scientific Instruments* is now also at this address.

New Patents.

THIS list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

Latest Patent Applications.

14777—Forst, P. von der.—Recovery of ammonia and ammonium compounds from gases. June 18th.

Specifications Published this Week.

216949—Cross, C. F., and Englestad, A.—Manufacture and applications of new lignone derivatives.

216982—Bruni, G.—Process for the production of phosphoric derivatives of inositol.

Abstract Published this Week.

214765—Amino anthraquinones.—Drescher, H. A. E., Thomas, J., and Scottish Dyes, Ltd., Murrell Hill Works, Carlisle.

Anthraquinoneimides of dibasic acids are obtained by heating a halogen-anthraquinone with an imide of dibasic acid in the presence of copper and an acid absorber; the latter may be omitted when a metal salt of the imide is employed. The imides yield amino-anthraquinones upon hydrolysis, for example, with concentrated sulphuric acid; by partial hydrolysis of phthalimidoanthraquinones, *o*-carboxybenzoylaminoanthraquinones are obtained. According to examples 1-phthalimidoanthraquinone is obtained from 1-chloranthraquinone and phthalimide with or without addition of nitrobenzene, and is hydrolysed with sulphuric acid to 1-aminoanthraquinone; unchanged halogen derivative may be removed at the hydrolysis stage by partially diluting the sulphuric acid solution and filtering; the following compounds are similarly obtained: 1:5-diphthalimido-, 1:5-diamino-, 1-chlor-5-phthalimido-, and 1-chlor-5-amino-anthraquinones from 1:5-dichloranthraquinone; 4-phthalimido- and 4-amino-1-methylamino-2-bromanthraquinone from 1-methylamino-2:4-dibromanthraquinone; 1-phthalimido-2-nitro- and 1-amino-2-nitro-anthraquinones from 1-chlor-2-nitroanthraquinone; 1-amino-2-methyl-4-phthalimido- and 1:4-diamino-2-methylanthraquinone from 1-amino-2-methyl-4-bromanthraquinone; *1-methyl-amino-4-phthalimido-* and methylamino-4-amido-anthraquinones from 1-methylamino-4-bromanthraquinone; 1-phthalimido-2-amino- and 1:2-diamino-anthraquinones from 1-chlor-2-amino-anthraquinone; 2-phthalimido-, 2-*o*-carboxybenzoyl-amino-, and 2-amino-anthraquinones from 2-bromanthraquinone; 1-succinimido-anthraquinone and a partial hydrolysis product thereof from 1-chloranthraquinone and succinimide. The production of amino-derivatives from 1:8-dichloranthraquinone, 1-chlor-4- or 5-nitroanthraquinone, and 1-chlor-4-oxyanthraquinones is also referred to.

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THE CHEMICAL NEWS,

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THE STRUCTURE OF SILICON.

BY HAWKSWORTH COLLINS, B.A. (CAMB.).

There is no reason why *all* the elements should be supposed to have been formed in an exactly uniform manner; and it is evident that such is not the case; for, if so, the regularity would have been discovered long ago. But there is also no reason why *some* of them should not have been formed in a regular manner; so that it is quite logical to take any, which show signs of regularity, totally ignoring the rest, and to investigate this appearance of uniformity.

The structure which has been obtained for an atom of silicon cannot be justified without taking into consideration facts with regard to all the elements in the second row o fthe Periodic Table.

(*a*) The only elements of atomic weight less than 36, from each of which a single electro-positive force is known to emanate, are Na(23), Li(7), H_3(3), and H(1).

(*b*) Each of the atomic weights of the seven elements from Na to Cl, inclusive, can he split up into as many parts, 23, 7, 3, 1, as *the element has valences. If the* atomic weight of each element had been one unit greater or less, not one of them could have been thus split up.

(*c*) If these parts are arranged so that ones always come in the even places and never in the odd places, and if the other numbers are arranged in the odd places in descending order of magnitude, the only *possible arrangement for each of the seven* elements is that given in Table I. In the case of Si (28) no other number between 17 and 31 inclusive can be split up in this manner into four parts.

TABLE I.

		At. Wt. divided into parts.	No. of parts.	Max. Val.
Na	23	= 23	1	1
Mg	24	= 23 + 1	2	2
Al	27	= 23 + 1 + 3	3	3
Si	28	= 23 + 1 + 3 + 1	4	4
P	31	= 23 + 1 + 3 + 1 + 3	5	5
S	32	= 23 + 1 + 3 + 1 + 3 + 1	6	6
Cl	35	= 23 + 1 + 3 + 1 + 3 + 1 + 3	7	7

The fact that Cl has an isotope (37) does not affect the truth of the table.

If, after this uniform arrangement has been obtained, any other regularity can be observed, the matter is placed far out of the region of chance, and can only be due to cause.

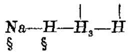
(*d*) Whenever there are present one or more helium-portions (1+3) or (3+1) the element is non-metallic, and whenever there is no such portion, the element is metallic.

The helium-portion (or portions) is called the non-metallic part of the element, and the remainder the metallic part.

(*e*) If electro-positive forces be understood to emanate from each portion of the metals, and also from each portion of the non-metallic parts of the non-metals, whilst electro-negative forces emanate from each portion of the metallic parts of the non-metals, the acidic and basic nature of each element is exactly explained.

(*b*) and (*c*) are regularities obtained by reasoning upon atomic weight and valency; (*d*) and (*e*) are regularities which are dependent upon (*b*) and (*c*) and could not have appeared if the latter were not exactly true.

Therefore the structure of an atom of silicon is:



where the three thin lines represent internal atomic bonds, the two thick lines electro-positive forces, and the two curved lines electro-negative forces. H_3—H is the non-metallic portion, and Na—H the metallic.

In a silicate (*e.g.*, Na_2SiO_3) the two

electro-positive valences combine with the two electro-negative valences of an atom of oxygen, and each electro-negative valence combines with an electro-positive base (ONa).

This structure for an atom of silicon will now be proved to be true quite independently of the above by means of the laws of relative volume and heat of formation.

TABLE II.

Relative Volumes of Silicon.

Si	=	Na	+ H	+ H_3	+ H
13.02	=	9.54	+ 0.97	+ 1.54	+ 0.97
17.61	=	11.85	+ 5.76	+ 0	+ 0
11.53	=	5.76	+ 5.76	+ 0	+ 0
7.13					
13.83		See Tables IV. and V.			
18.91					

5.76, 9.54 and 11.85 frequently appear as volumes of Na. 5.76 is the commonest volume of H.

TABLE III.

Relative Volumes of Al, Si, P & S compared.

	Na + H + H_3 + H + H_3 + H
Al	12.05 = 9.54+0.97+1.54
Si	13.02 = 9.54+0.97+1.54+0.97
P	14.56 = 9.54+0.97+1.54+0.97+1.54
S	15.53 = 9.54+0.97+1.54+0.97+1.54+0.97

TABLE IV.

Experimental Data illustrating the Volumes of Table II.

	Relative Volumes.	Theor S.G. at 15° C.	Obs. S.G.	
(141)	MnSi 6.94 + 7.13	5.90	5.90	15° Nostrand
(142)	$MnSi_2$ 6.94 + 2(7.13)	5.24	5.24	13° Nostrand
(143)	SiC 7.13 + 5.69	3.12	3.12	15° Nostrand
(144)	FeSi 6.4 + 7.13	6.21	6.17	Pick and Conrad
(145)	$FeSi_2$ 6.4 + 2(7.13)	5.42	5.4	Pick and Conrad
(146)	Fe_2Si 2(6.4) + 7.13	7.03	7.0	Pick and Conrad
(147)	Fe_3Si_2 3(6.4) + 2(7.13)	6.7	6.7	Pick and Conrad
(148)	Fe_6Si_2C 6(6.4) + 2(7.13) + 8	6.66	6.6	Colson
(149)	Si 11.53	2.43	2.34	Miller
			2.48	Playfair
(150)	Si 13.83	2.025	2.004	- 2.194 Winkler
(151)	$Na_2SiO_3 + 8H_2O$ 2(11.85) + 13.83 + 4.45 + 2(2.51) + 8(14.03)	1.67	1.666	18° F. W. Clarke
(152)	$BaSiO_3$ 24.58 + 13.83 + 4.45 + 2(2.51)	4.43	4.44	18° Nostrand
(153)	Na_2SiF_6 2(11.85) + 13.02 + 6(5.42)	2.715	2.75	17° Stolba
			2.69	Schroder
(154)	$CaSi_2$ 12.24 + 2(13.02)	2.508	2.5	Nostrand
(155)	$AlNaSi_2O_6$ 9.05 + 11.85 + 2(13.02) + 6(2.51)	3.26	3.26	Damour
(156)	Al_2SiO_5 2(9.05) + 13.02 + 5(2.51)	3.71	3.678	Jacobson
(157)	$Al_2SiO_4F_2$ 2(9.05) + 13.02 + 4(2.51) + 2(5.42)	3.54	3.514	to 3.563 Rammelsberg
(158)	K_2SiF_6 2(18.05) + 13.02 + 6(5.42)	2.69	2.704	Schroder
			2.665	17°.5 Stolba
(159)	SiO_2 17.61 + 2(2.51)	2.651	2.651	Breithaupt
(160)	$FeSiO_3$ 10.08 + 17.61 + 3(2.51)	3.748	3.713	Gruner
(161)	$SrSiO_3$ 19.56 + 17.61 + 3(2.51)	3.669	3.652	25°/4 Nostrand
(162)	$SiBr_4$ 18.91 + 23.09 + 3(27)	2.83	2.813	0° Pierre
(163)	SiO_2 18.91 + 4.45 + 2.51	2.319	2.317	Rose
			2.322	Ullik
(164)	$CaSiO_3$ 13.25 + 18.91 + 3(2.51)	2.923	2.919	18° Nostrand

TABLE V.

	Heat of Formation of Silicon.	Original Volume		Rel. Vol. in combination at 15° C.		Change of Volume
(a)	-24797 = 120 × (-7.38) × 28	11.53	=	18.91	-	7.38
(b)	-12701 = 120 × (-3.78) × 28	13.83	=	17.61	-	3.78
(c)	0 = 120 × 0 × 28	13.83	=	13.83	-	0
(d)	-17069 = 120 × (-5.08) × 28	13.83	=	18.91	-	5.08
(e)	22512 = 120 × 6.7 × 28	13.83	=	7.13	+	6.7
(f)	-7728 = 120 × (-2.3) × 28	11.53	=	13.83	-	2.3

The following examples illustrate the six different cases of Table V.:

(a) H.F. of $SiBr_4$ is − 24797 + 45244 + 3(17000) = 71447 71000 (obs.). This corresponds exactly with No. 162, Table IV.

(b) H.F. of SiO_2 is − 12701 + 2(96155) = 179609. 180000 (obs.). This corresponds exactly with No. 159, Table IV.

(c) H.F. aq. of Na_2SiO_3 is 2(31234) + 0 + 71515 + 2(96155) = 326293. 326100 (obs.). This corresponds exactly with No. 151, Table IV. 31234 is sometimes the H.F. aq. of Na, slightly less than the H.F. solid 32706 demonstrated in *The Chemical News*, 1924, CXXVIII., 161.

(d) H.F. of $CaSiO_3$ is 59568 − 17069 + 3(96155) = 330964. 329350 and 344400 (obs.). This corresponds exactly with No. 164, Table IV.

(e) The Heat of Formation of SiC, if the C was obtained from diamond, is 22512 − 21465 = 1047. 1963 and 2000 (obs.). H.F. of C is − 21465 = 795 × (−2.25) × 12. 3.44 (diamond) = 5.69 − 2.25. This corresponds with No. 143, Table IV.

(f) H.F. of $BaSiO_3$ is 72134 − 7728 + 71515 + 2(96155) = 328231. 328100 (obs.). This corresponds exactly with No. 152, Table IV.

13.02 is the commonest volume of Si, but it does not happen to have existed in any compound of which the H.F. was directly obtained by experiment.

SUMMARY.

In finding the structure of an atom of silicon and proving the same to be true, four laws are employed and thereby strengthened:—

(1) *The Law of the Formation of Non-Metals.*—The non-metallic nature of an element is always due to a pair or pairs of electro-positive forces, each pair emanating from a portion of the element, of which the mass is 4, taking the mass of an atom of hydrogen as unity.

(2) *The Law of Electro-Positive and -Negative Valences.*—The valences which emanate from the metallic portions of non-metals are electro-negative; all other valences are electro-positive.

This law has never been stated before, although facts demonstrating it have frequently appeared in *The Chemical News*. For its application to oxygen and fluorine, see *The Chemical News*, 1924, CXXVIII., 230.

(3) *The Law of Relative Volume.*—The relative volume of an atom is the sum of the relative volumes of its parts, any one or more of which may be zero.

(4) *The Law of Heat of Formation.*—The heat of formation of an element is proportional to the product of the atomic weight and the change of volume; there being two distinct series, the sodium elements and the sub-sodium elements.

SPIRO COMPOUNDS WITH REFERENCE TO FORMATION AND STABILITY.

PART III.—SPIRO COMPOUNDS FROM CYCLOHEPTANE AND BRIDGED SPIRO COMPOUNDS FROM CYCLOPENTANE.

BY R. F. HUNTER, B.Sc., A.R.C.Sc., M.S.CHIM., F.C.S.

The main result of the researches which have been carried out by Profs. Thorpe and Ingold and their collaborators at South Kensington during the last ten years has been to confirm the view as to the manner in which change of the normal angle between two valencies of a carbon atom tends as a consequence also to deflect the two remaining valencies. Two effects have been examined: firstly, that which depends on the combined volume of two atoms or groups attached to the carbon atom, and secondly, that which depends on the inclusion of two valencies in a ring.

Now at this point it became clear that it was necessary to examine more closely the individual cases in which real or apparent exceptions to the general hypothesis might possibly be found, and, with this object in view, three sets of experiments were commenced, firstly experiments on the effect of the indirect attachement to a carbon atom of groups of considerable atomic volume; secondly experiments on the dependence of the influence exerted by groups on their electrical character, and lastly experiments on the effect of including two valencies of a carbon atom in rings containing a large number of atoms. The original hypothesis of Ingold, Beesley and Thorpe (*loc. cit.*), namely, that when two valencies of a carbon atom are included in a ring, the remaining two dispose themselves in such a way as to divide up the space external to the ring as equally as possible, leads to the result that an increase in the number of carbon atoms composing the ring is accom-

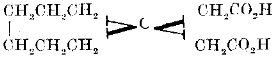
panied by a continuous decrease in the inclination between the external pairs of valencies, and a continuous increase in the ease with which the second ring can be closed by the elimination of groups attached to the acetic residues is to be looked for as a homologous series is ascended.

It is important, however, to notice that these conclusions are based on the supposition that the angles between each pair of valencies composing homocyclic rings are actually the internal angles of the corresponding uniplaner polygons.

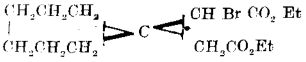
Now, in large rings, such as cycloheptane and cyclo octane rings, a means exists whereby the internal angles of the ring can adjust themselves more nearly to the minimal strain, namely, by free rotation around individual bonds composing the ring of such a kind as to lead to configurations in which the atoms of the ring occupy two or more planes. It is, of course, neither necessary nor desirable to assume that any particular configuration of any kind would in any sense have a permanent character, any more than that the favoured configurations which almost certainly exist in saturated open chain compounds capable of executing free rotations about single bonds represent permanent configurations of these molecules, especially since at all temperatures above absolute zero partial or complete relative rotations of the type suggested will presumably be one of the kinds of motion contributing to the internal energy. Nevertheless, on general grounds, it is reasonable to suppose that the more the internal angle of the uniplaner ring diverges from the angle of no strain, the more will that ring, by motion compounded of rotations about the individual bonds, tend to pass through multiplaner configurations, and the more, therefore, will the effective mean value of the internal angles of the ring fall below the maximal value which the angle reaches when the ring is uniplaner.

Reverting again to the hypothesis of Ingold, Beesley and Thorpe, it is not to be expected in the case of the cycloheptane ring, and still less in the cyclo octane ring, that the angle between two valencies external to the ring is actually as small as the simple calculation indicates. Indeed, it would be unsafe to assume any continuous decrease in the external angle takes place on passing from cyclopentane to cyclo otcane. Cycloheptane and cyclo octane might occupy anomalous positions, resembling cyclopentane rather than cyclohexane so far as concerns the transmission of strain to attached groups or rings, if the conditions are such that multiplaner configurations are predominant. The theoretical problem underlying these considerations is quite insoluble in the absence of more exact knowledge of the forces which give rise to favoured configurations around single bonds and of the manner of distribution of the energy of such motion.

Baker and Ingold carried out experiments with derivatives of cycloheptanediacetic acid (*Jour. Chem. Soc.*, 1923, CXXIII., 122), and demonstrated that in the cycloheptane ring there certainly appears to exist some condition which greatly reduces the strain within the ring, and therefore the convergence towards one another of the two acetic acid residues. So much in this case that the effect of the cycloheptane ring in promoting the formation and enhancing the stability of spirane structures such as spirocyclopropane acid (1) is not only less than it might be expected to be, but is actually somewhat less than that which the cyclohexane ring would exert.

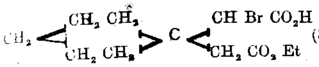


(1)



(2)

In many respects, however, the experiments of Baker and Ingold yielded results very closely allied to those obtained by Thorpe, Beesley and Ingold in the cyclohexane series. Thus in the cycloheptane series, it was found impossible to prepare the monobromo neutral ester (2), although in the cyclopentane and gem dimethyl series the corresponding compound was readily isolated. On the other hand there was experienced no difficulty in isolating the monobromo acid ester which was obtained in considerable quantity when the Hell Volhard Zelinsky bromination product was poured into alcohol. A similar substance was obtained in the cyclohexane series, but it was a syrup which could not be purified, and the conclusion that it was (3) was based on hydrolysis.


(3).

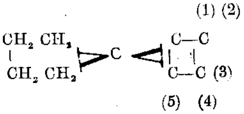
In the cycloheptane series, however, the monobromoacid ester was a well-defined crystalline solid, so that there can be no question as to its composition, although there is no evidence as to which of the two carboxyls is esterified. Again, just as in the cyclohexane series, the dibromo ester is unstable, since on heating it passes into the bromo lactone ester with the elimination of ethyl bromide.

The same remarkable tendency to yield a lactone was not observed in the neutral dibromo esters of the gem dimethyl and cyclopentane series, and it is a clear indication of the enhanced tendency in the cyclohexane and cycloheptane series towards the formation of rings by the elimination of groups from the two acetic acid residues. On hydrolysis of the monobromoacid ester with concentrated aqueous alkali at 150°, hydrogen bromide was eliminated with the formation of the spiro acid (1), the yield being nearly the same as in the cyclohexane series.

Certain remarkable differences between the two series were, however, observed during the investigation of the stability of the spiro acid (1) towards mineral acids. Caronic acid, which is the analogue in the gem dimethyl series, readily undergoes fission at 200° with 5 per cent. hydrochloric acid, and the cyclopentane analogue is also completely decomposed under these conditions, although an analogue of terebic acid was not isolated in this case (*J.C.S.*, 1920, CXVII., 1579). The cyclohexane spiro acid, on the other hand, is extremely stable, and survives heating at 240° with 20 per cent. acid for six hours. The stability of the cycloheptane spiro acid was found to lie between that of the cyclohexane and the cyclopentane acid.

The investigation of the products of hydrolysis of the bromolactone ester afforded further evidence that the cycloheptane spiro compounds are not so readily formed nor are they generally so stable as the corresponding cyclohexane derivatives, and in that respect, the cycloheptane compounds appear to occupy a position intermediate between the cyclopentane and cyclohexane series. In the cyclohexane series the bromo lactonic ester was obtained in cis and trans forms, which, on hydrolysis with 64 per cent. potash, gave a hydroxyspiro acid. This hydroxy acid was not isolated in the cyclopentane series. In the cycloheptane series, however, the hydrolysis of the bromo lactone ester gave a small quantity of corresponding hydroxy spiro acid.

It will be recalled in Part 1. of this sereis, with reference to the paper of Profs. Thorpe and Ingold, published in 1919, that it was found that the principal influence exerted by the cyclohexane ring consisted in the diminishing the stability of the spirocyclo propane bonds (1:5) and (4:5), whilst the second order effects appeared in the more remote parts of the molecule. The curious fact that the spirocyclopropane bonds should be stabilised by the cyclohexane ring in the cyclohexanespirocyclopropane system, but rendered less stable in the bridged cyclohexanespiro compound, received ready explanation on the lines of the original hypothesis, which also accounted in a natural manner for all the subsidiary effects, and in view of the agreement with theory and the possibility which it opens of predicting the susceptibilities of complex systems of associated rings, it seemed desirable to carry out the obvious tests with the compounds derived from the cyclopentane structure (4).


(4)

The angle of the cyclopentane ring is very close to that at which two valencies emerge from a carbon atom in the unstrained condition, and hence the above structure should resemble the corresponding gem dimethyl structure, rather than the corresponding cyclohexanespiran structure, in all respects in which these latter differ from one another. Thus, the bond (5:1) in (4) should be as stable as it is in the gem dimethyl compound, and not singularly unstable as it is in the cyclohexane analogue, whilst as regards the bonds (1:4) and (3:4), the second order diminutions of stability, noticed in the case of the cyclohexane derivatives, should not appear. With this in view, an investigation on the bridged spiro compounds from cyclopentane was undertaken by Thorpe, Ingold and Lanfear (*Jour. Chem. Soc.*, 1923, CXXIII., 3140), and it can be stated that each of the predictions of

the theory is in accordance with the facts which emerged in the course of this investigation.

The most remarkable contrast with the cyclohexane series was observed in experiments designed to test the susceptibility to fission of the bond (5:1). The fission of this bond was brought about with great ease in certain substances in the cyclohexane series by alkaline reagents which were without effect on the corresponding compounds in the gem dimethyl series. When the cyclopentane derivatives were examined, they were found to be just as stable as the gem dimethyl compounds, and to resist the attack of reagents which completely decomposed their ring homologues of the cyclohexane series. Evidence regarding the secondary influence on the bond (3:4) was also obtained. The expected effect is in the nature of a small increase in stability when the comparison is made with the cyclohexane series, the cyclopentane structure closely resembling the gem dimethyl structure. Owing to the smallness of the effect, and to experimental difficulties arising from the instability of the bond (5:1) in the cyclohexane series, a reagent was not found which was capable of bringing about the fission of the bond (3:4) in one series and not in the other. The establishment of the bond (3:4) was, however, examined. A process in which the influence of the cyclohexane ring, as transmitted through the bonds of the cyclopropane ring, is magnified sufficiently to render it capable of easy detection. The result of a series of comparative experiments was to show that the closure of the cyclobutane ring by the establishment of the bond (3:4) proceeds much more smoothly in the cyclopentane series than in the cyclohexane series, and that in this respect the cyclopentane compounds closely resemble the gem dimethyl derivatives.

The bond (1:4) undergoes fission in certain corresponding acids of all three series when these acids are treated with sodium amalgam, two atoms of hydrogen being added to the molecule. It was to be expected that in the cyclopentane series, this reaction would proceed much as it does in the gem dimethyl series, that is to say, considerably less easily than when cyclohexane derivatives are employed. Comparative experiments with acids of the three series showed that this is the case, and that the reaction velocities are related to one another in the manner which the hypothesis of strain transmission requires.

The bridge compounds were synthesised as in the earlier investigation (*loc. cit.*), that is to say, cyclopentane 1:1 diacetic acid was brominated and the dibromo ester converted by treatment with ethyl sodiomalonate into a cyclopentanespirocyclopropane ester, from which the bridged ring sodio ester was prepared by the application of the Dieckmann reaction.

$$C_4H_8 : C < \begin{array}{l} CH\,Br\,CO_2\,Et \\ CH\,Br\,CO_2\,Et \end{array}$$

(5)

$$\rightarrow C_4H_8 : C < \begin{array}{l} CH\,CO_2Et \\ | \\ C\,(CO_2Et)\,CH\,(CO_2Et)_2 \end{array}$$

(6)

$$\rightarrow C_4H_8 : C < \begin{array}{l} C\,(CO_2Et)\,C \cdot CO_2Et \\ | \qquad\qquad\quad \| \\ C\,(CO_2Et)\,CO\,Na \end{array}$$

(7)

Both the dimethyl and cyclohexane bridge ring compounds can be prepared directly from the corresponding dibromo esters by treatment with ethyl sodiomalonate in the presence of sodium ethoxide. In the former case the reaction proceeds fairly smoothly, the maximal yield of the required compound being about 65 per cent. In the latter case the second stage of the reaction is rather difficult to bring about, and the yield of the bridged ring compound only about 25 per cent. Experiment has shown that in the cyclopentane series the reaction can be brought about in one operation, and that it proceeds fairly smoothly to yield the bridged compound in about 63 per cent. yield, and therefore nearly the same as the gem dimethyl series. To make the comparison more definite, the cyclopentanespirocyclopropane ester (6) was isolated and converted by treatment with sodium ethoxide into the bridged ester (7). The corresponding reaction in the gem dimethyl series leads to the formation of the bridge ring compound in 70 per cent. yield after three hours at 75° C. and a maximal yield of 75 per cent. after five hours. In the cyclohexane series, the closure of the ring is more difficult, and the yield of the required compound was only 23 per cent. and 29 per cent. respectively ater three and five hours' heating at 75° C. In the cyclopentane

series a yield of 70 per cent. was obtained after two hours' heating at 75° C., and a yield of 73 per cent. after four hours' heating, so that there can be little doubt that the cyclopentane series resembles the gem dimethyl series rather than the cyclohexane series as regards the establishment of the bond (3:4).

Evidence of a marked difference in stability between the bridged spiro compounds of the cyclopentane and cyclohexane series was obtained in the course of experiments on the action of alkaline hydrolysing agents on the compound (7). The action of cold alcoholic potassium hydroxide on the cyclopentane sodio ester (7) yields a well defined dipotassium derivative; further hydrolysis leads to a singularly stable dibasic ester, which remains unattacked under conditions in which the corresponding compound in the cyclohexane series is completely decomposed.

The first action of mineral acids on the sodio compound (7) is to convert it into the free enol ester. Further hydrolysis proceeds in a number of more or less definite stages with the production of an acid ester, a dicarboxylic acid, and a monocarboxylic acid (*J.C.S.*, 1923, CXXIII., 3140). Further degradation of the structure can be brought about with the aid of reducing agents which readily effect the fission of the bond (1:4) in the monocarboxylic acid. The product is cyclopentanespirocyclopentanonecarboxylic acid, and its constitution follows from its oxidative degradation with nitric acid to a mixture of cyclopentane 1:1 diacetic acid and cyclopentane 1 acetic 1 carboxylic acid. The reduction of the bridged monobasic acid of the cyclohexane series to its unbridged derivative occurred with considerably greater ease than in the gem dimethyl series. This was established by a series of comparative experiments, which showed that, under the conditions employed, the reduction of the cyclohexane compound proceeds about 1.8 times as fast as that of the gem dimethyl compound. On extending this to the cyclopentane series, it was shown that reduction takes place at about only half the rate that it takes place at in the cyclohexane series, and the velocity of reduction was, in fact, very close to that found in the case of the gem dimethyl series.

Thus, in three separate instances of ring closure or ring fission, namely, the closure of the bond (3:4), and the fission of the bonds (4:5) and (1:4), the hypothesis of strain transmission has correctly predicted the susceptibilities of the structure under investigation.

Highbury New Park, N.5.
June, 1924.

GENERAL NOTES.

IODINE AND POTASSIUM SALTS FROM SEAWEED.

The technical papers of the Fuel Research Board form a series of reports on the results of work carried out for the Board at H.M. Fuel Research Station or elsewhere.

A paper on the "Carbonisation of Seaweed as a Preliminary to the Extraction of Iodine and Potassium Salts,"* gives the results of an investigation carried out at H.M. Fuel Research Station, at the request of the Development Commission, to ascertain the possibilities of extracting iodine and potassium salts from seaweed by means of a carbonisation process in closed retorts.

It is considered that the data obtained from these experiments may be useful in the devising of a self-contained system of carbonisation whereby the kelp-weeds can be dealt with in such a way as to avoid loss of iodine, the gaseous products being utilised for the firing of the necessary retorts.

—From the *Board of Trade Journal*, July 10, 1924.

The American Oil Chemists' Society has established an official publication, a quarterly, to be published from the same press which prints the publications of the American Chemical Society. This chemical publication, *The Journal of the Oil and Fat Industry*, will be devoted to the science and chemistry of vegetable oils, animal fats, and fish oils, and other glycerides, waxes, and lipoids. Papers will be accepted for publication if they involve

* *By J. G. King, B.Sc., A.R.T.C., F.I.C. Published by H.M. Stationery Office. Price 6d. net.*

original work, or news notes, on the production, refining, utilisation, analysis, composition, constants, synthesis, purification, statistics, or other information on oils and their by-products.

Among the by-products which will be considered are the oil meal feed and fertilisers, soaps, paints and varnishes, fatty foods, fish oils, pharmaceuticals, lubricants (where glycerides, etc., are concerned), and any instance where oils and fats are concerned.

The editorial board is headed by Dr. Herbert Bailey, of the Southern Cotton Oil Company (vegetable oil producers and refiners and paint manufacturers), and is composed of the leading chemists in this field in America.

The *Journal of the Oil and Fat Industry* will be published in January, April, July and August. Subscription for the first six issues, composing volumes I. and II., is $3.50 ($3.75 outside the United States); succeeding volumes will cost $2.50.

Orders for subscriptions should be sent to Fred H. Smith, Managing Editor, Experiment, Georgia, U.S.A.

PROCEEDINGS AND NOTICES OF SOCIETIES.

IRON AND STEEL INSTITUTE.

The Autumn Meeting of the Institute will be held at the British Empire Exhibition, Wembley, on Thursday and Friday, September 4 and 5, at 10.30 a.m. each day.

The following papers have been offered for discussion:—

L. Aitchison and G. R. Woodvine: *Changes of Volume of Steels during Heat Treatment.*

C. Benedicks and V. Christiansen: *Investigations on the Herbert Pendulum Hardness Tester.*

E. D. Campbell and G. W. Whitney: *The Effect of Changes in Total Carbon and in the Condition of Carbides on the Specific Resistance and on some Magnetic Properties of Steel.*

C. A. Edwards: *Pickling: The Action of Acid on Iron and Steel, and the Diffusion of Hydrogen through the Metal.*

J. Newton Friend and W. E. Thorneycroft: *Examination of Iron from Konarak.*

M. A. Grossman and E. C. Bain: *On the Nature of High-Speed Steel.*

Axel Hultgren: *Improvements in the Brinell Test on Hardened Steel, including a new method of producing Hard Steel Balls.*

W. Rosenhain: *Present position of the Theories of the Hardening of Steel.*

F. C. Thompson and W. E. W. Millington: *The Effect of Free Surfaces on the Plastic Deformation of Certain Metals.*

THE FARADAY SOCIETY.

At the Annual General Meeting, held on July 7, Professor F. G. Donnan, C.B.E., F.R.S., was elected to succeed Sir Robert Robertson as President. The Annual Report records considerable activity during the past year, the result of which is reflected in the accounts, which show a deficit of £109 11s. 5d. on the year's work. Eleven meetings were held during the year, and of these, four were General Discussions, which have become so striking a feature of the work of the Society. The subjects of these were as follows: I., *Alloys Resistant to Corrosion;* II., *The Physical Chemistry of the Photographic Process;* III., *The Electronic Theory of Valency;* IV., *Electrode Reactions and Equilibria.* The widespread appreciation in which the publications of the Society are held is indicated in the fact that the sales of Transactions and reprints amounted to nearly £900, a figure in excess of the amount received for subscriptions. It is surprising to note that the membership of this very active Society is only 432, and that consequently an appeal for a larger membership is made in the Annual Report. Particulars relating to the Society may be obtained from the Secretary and Editor, Mr. F. S. Spiers, 90, Great Russell Street, London, W.C.1.

MODERN ALCHEMY.

It is announced in Berlin that two German professors have succeeded in synthesising gold from mercury, and will shortly publish their results. The cost of electric current is, however, prohibitive, but the professors have taken out patents for their process.

SOCIETY OF CHEMICAL INDUSTRY.

At the Annual General Meeting, held on July 9, the Presidential Address was delivered by DR. E. FRANKLAND ARMSTRONG, F.R.S.

The year which has elapsed since we met at Cambridge may be regarded justly as a period of steady progress towards the realisation of those ideals of co-operation which many of us consider essential before the chemical profession can attain the status which all chemists claim for it. In spite of this progress, however, the position, to my mind, is still one of considerable anxiety, as there are certain indications of increasing competition between the chemical societies such as is bound to have a serious effect on their financial position if it is not checked. It is more than ever urgent that the energies of those who take an active part in such matters, and they are all too few in number, should be directed to a common object and not dissipated in rival schemes.

The outstanding achievement of the year is indubitably the collective exhibit of the British Chemical Industry at the Wembley Exhibition, including the scientific section. For once—a portent for the future—Chemistry has been first in the field. Our Manufacturers' Association was the first to agree to a collective exhibit, and we are the only industry to associate our science so definitely with our trade exhibits. It is a subject for congratulation that the latter part of the scheme originated with our council, and that the success of the scientific exhibition is largely due to the energy put into the scheme by Dr. Levinstein, our representative on the joint committee and its chairman. It is difficult to find words to commend the work put into everything connected with Wembley by our President-elect, Mr. Woolcock—for those of us who know him it is most accurate to express our appreciation by saying he has enjoyed it. The scientific publications associated with the Exhibition have particularly been the work of our Society, and they form a precedent which I personally hope will often be followed. The popular pamphlets are a real necessity, and we must have more of them. Our book, "Chemistry in the XXth Century," is an achievement of which all chemists can feel proud: it can seldom habe heen the lot of an editor to find so many willing helpers. Lastly, a word of grateful recognition is due to Messrs. Benn Bros., for their enterprise in publishing our productions: it is improbable that a book of this size and nature was ever put more quickly through the press.

Altogether we may feel proud of Wembley and our share in it: may I hope further tbat we record faithfully the lessons we shall learn from our experience, as I am convinced that much more has to be done by us, both collectively and individually, than in the past to educate both the nation and the individual to the importance and indeed the very meaning of the chemist and his knowledge.

The report of your council details the chief happenings of the year, so that I need only refer very briefly to one or two events of outstanding interest. The formation of the Bureau of Chemical Abstracts, under the chairmanship of Prof. J. C. Philip, is perhaps the first step in the unification of all British chemical publications. Composed of representatives of the Chemical Society and our own Society, it is aiming to secure uniformity in the abstracts on pure and applied chemistry published by the two societies, to prevent any overlap, and to explore the possibility of further co-operation. Progress must necessarily be slow, steps once taken cannot easily be retraced, and the problem is the more complex on account of the financial considerations involved. We look to the Bureau during the next five years to unify transactions as well as abstracts and to bring the publications of other societies within its scope. No paper should be abstracted more than once in British literature. It should not be impossible to meet the desire of the smaller specialist societies for more general papers, not always containing new matter, and for fuller abstracts than are at present supplied: it must be remembered that many of their members are not chemists in the strict sense of the word. Our weekly journal, *Chemistry and Industry,* will facilitate the publication of general papers, and it should not be impossible to abstract all papers dealing with the glass industry, for example, such as now appear under Group VIII. in our abstracts, once a month, the section being sent by itself to members of the particular society. I attach the greatest importance to the magic of "together"; we must have hoth ideas and ideals.

The Federal Council must this year play an active part in bringing us together: the representatives of the societies on it must

not hold a watching brief, but be prepared actively to engage in constructive effort. I venture to suggest that a definite constructive programme be drawn up by the Federal Council this autumn, or sooner, if it be possible, that it be submitted to the constituent societies for their approval before Christmas, so that the way is cleared for immediate action in 1925. I must confess to a feeling of disappointment that the proposals I put forward in outline a year ago have not yet been examined either by the Federal Council or by the various Chemical Societies. Still I realise that in the chemical world things move slowly for various reasons; and it is a source of satisfaction that, in this and some other instances during my term of office as President, seeds have been sown which may lead to important results, although there is but little to show at the moment to some of us.

The most obvious next step towards the consolidation of the chemical profession is the establishment of Chemistry House, where a common meeting ground can be found for most of our societies, and the way made easy for closer co-operation. Such a scheme has long been a dream of the future with many of us: its realisation has been brought nearer by the munificent bequest of the late Mr. Leonard. What I consider to have been a practical scheme was under discussion in the opening months of this year, and I cannot help the feeling that had a little more energy been displayed and a real desire evinced to establish a home, we might by now have been in possession of it under advantageous financial conditions.

During this last year the scheme has received an important impetus; it is for my successor in office and for the general body of chemists, especially the younger ones, to maintain this impetus and accelerate it. So long as the matter is not allowed to drift I shall be well satisfied.

The desiderata for our first scheme are:

(1) Office accommodation in one building in a convenient central position for the administration of the Chemical Society, Society of Chemical Industry, Association of British Chemical Manufacturers, Institution of Chemical Engineers and such other Societies, including the Institute of Chemistry, as are willing to take part.

(2) Suitable council and committee rooms, so that all such meetings can be held in the one building.

(3) Social meeting rooms, so that the Chemical Industry Club can definitely be asociated with Chemistry House from its inception.

(4) Offices for the Bureau of Chemical Abstracts and all other journals issued by the participating societies.

(5) A lecture theatre sufficient for all but the very large meetings.

It is believed that suitable premises could be obtained at a capital cost which is within the range of practical politics.

The ultimate larger scheme which is at present far beyond our realisation would include, in addition to the above, a library, full accommodation for a club including bedrooms and a restaurant, and also for the Institute of Chemistry which is not mentioned more specifically in the foregoing, since it already possesses its own house.

We meet this year in Liverpool, commercially one of the centres of the world. By river, canal, road and rail, the products of industrial Lancashire and Yorkshire are brought to its wharfs to be carried by its ships to all the countries of the world—the ships bring back with them raw products of every kind which pass into Lancashire and Yorkshire to be manufactured. Liverpool has made much of its opportunities, its citizens are justly proud of their city, of its civic and corporate life and of its University whose hospitality we are enjoying today. The very existence of the University, munificently endowed by local generosity, though its needs are still many, proves the recognition which Liverpool gives to science. That our science in particular is not forgotten is shown by the fact that there are, or soon will be, five chairs in Chemistry here. Chemical science is also represented locally by active sections of our own society and of the Institute of Chemistry. If such a gathering as this may leave a message behind it, surely, in congratulating Liverpool on all that it has achieved in the past, in honouring its many great traditions, we may urge it in the future to redouble its encourage of science and the prosecution of scientific research, and to be ever zealous in applying the results of science for the service of its citizens.

The President took for his address: *A Neglected Chapter in Chemistry: The Fats*, embodying work by himself and Mr. John Allan.

This account of our knowledge of the fats

and of some of the many problems needing study, particularly in the organic branch of chemistry, is mainly written with the hope of reviving interest in them as, apart from physical and analytical investigation, no other province of chemistry has been so litle studied during recent years. This is, no doubt, almost entirely due to the considerable experimental difficulties which confront the worker and to the need for making a mass attack on the subject by the whole staff of a research school during a number of years before any measure of success can be obtained. It is our intention mainly to consider the subject from the point of view of the origin and the significance of the fats—botanist, chemist, and physiologist alike have an interest in this question. We shall strive to indicate what has been already established as well as the lacunæ in our knowledge. We shall propound questions and seek answers, thereby hoping t ostimulate the interest of our colleagues.

I.—The Fatty Acids.

As is well known, the natural fats, both animal and vegetable, are usually triglycerides of straight-chain fatty acids in which all three hydroxyl groups of glycerol are acted upon either by the same or by different fatty acids, the product being termed either a simple or a mixed glyceride. Fatty diglycerides do not normally occur as such, but they may be formed by fermentative action. The place of one or more of the fatty acid radicals may be taken, however, by an acid of a different kind, as, for example, phosphoric acid in the case of lecithin. Other alcohols besides glycerol are ound associated with fatty acids. They constitute the waxes, which are mixtures of esters of monohydric alcohols with the fatty acids of high molecular weight and occur as a rule in other parts of the plant than the fats, which are practically confined to the fruits and seeds. Their function seems to be that of protection against water, and not that of a reserve energy-producing material. In lecithin the third hydroxyl group of the glycerol is coupled by an ester union with phosphoric acid: It will be clear that the opportunity for isomerism and stereoisomerism in this group is large, and that the number of possible arrangements even of such apporently simple materials as glycerol and a few fatty acids is considerable.

We are once more brought face to face with the variety which nature is able to evolve from apparently simple materials. We shall use the term fats as covering both the solid fats and the liquid oils; it avoids confusion often present in the lay mind, resulting from the use of the term "oil" for mineral and essential oils.

The fatty acids which occur in nature in the fats as glycerides range from C_4 to C_{24}, inclusive. It is a remarkable fact that only acids with an even number of carbon atoms are present; this fact will be discussed further later.

The waxes contain still higher saturated acids and range from C_{14} to C_{30}.

Both saturated and unsaturated acids occur, some fats—liquid oils—being particularly unsaturated and liable to undergo change. A special class contains an hydroxyl group; in it occur both saturated and unsaturated forms.

Lastly there are the cyclic acids of the chaulmoogric series.

A brief summary of the chemical structure of some of the members of each group seems desirable to facilitate the understanding of the second portion of the paper; it will show the many gaps in our knowledge.

The saturated acids, CnH_2nO_2.

The saturated acids call for little comment—they all contain a straight chain of carbon atoms, and no isomerism is possible; they crystallise in one form only, the crystal unit being composed of two molecules arranged end to end with the carboxyl groups adjacent to each other. It is of interest that the synthetic acids containing an odd number of carbon atoms in this series are many of them enantiotropic—they have two melting points and crystallise in two forms. This difference is ascribed by Garner and Randall to alternative methods of arrangement of the two molecules of the acid which go to make up the crystal unit.

The unsaturated acids, $CnH_2n{-}_2O_2$.

Myristoleic acid, $C_{14}H_{26}O_2$, has been isolated by Tsujimoto as a constituent of sperm and dolphin oils, being chiefly responsible for the iodine absorption of the lower fractions of the methyl esters. It is shown to have the structure:

$CH_3 \cdot [CH_2]_7 \cdot CH{:}CH \cdot [CH_2]_3 \cdot CO_2H.$

It is of interest that the ethenoid bond is

in the same position with regard to the CH_3 group as it occupies in oleic acid as well as in erucic acid.

Palmitoleic acid, $C_{16}H_{30}O_2$, is not a common constituent of oils, at any rate in other than very small amounts, but it occurs in greater quantity (17 per cent.) in whale oil, from which it can be separated in almost pure state, and to the extent of 12 per cent. in skin grease. It gives a solid iso-acid melting at 21-22° under the same experimental conditions as oleic acid forms elaidic acid. Thepos ition of the ethenoid bond in it is unknown.

Oleic Acid.—This acid is characteristic of every fat, and its presence gives to the fats some of their best-known attributes. A number of isomerides are theoretically possible according to the position occupied by the ethenoid bond; there is also the possibility in each instance of *cis-trans* geometrical isomerism.

Several isomeric oleic acids, $C_{18}H_{34}O_2$, have been described, *viz.*:—

(1) Ordinary oleic acid, which has the ethenoid bond in the middle of the chain between carbons 9 and 10, counting the CO_2H group as 1. It has the formula:

$$CH_3 \cdot [CH_2]_7 \cdot CH : CH \cdot [CH_2]_7 \cdot CO_2H.$$

(2) Hepatic oleic acid, 12:13, was identified by Hartley as having the structure:—

$$CH_3 \cdot [CH_2]_4 \cdot CH : CH \cdot [CH_2]_{10} \cdot CO_2H.$$

(3) Iso oleic acids of unknown constitution are formed during the distillation of commercial stearin or during hydrogenation of oleic acid. Moore has provisionally ascribed an 11:12 ethenoid structure to one of these.

(4) Oleic acid, 2:3, was prepared by Le Sueur from stearic acid.

(5) Elaidic acid, m.p. 44.5°, which is the geometrical solid isomeride of liquid 9:10-oleic acid.

It is customary to describe oleic acid as the *trans* acid for reasons of which we must plead ignorance, though it is usual in other cases of geometrical isomerism, in the absence of any definite evidence, to regard the more stable higher-melting form as the *trans* isomeride, which would therefore lead us to assign this structure to elaidic acid. The latter is obtained by the action of nitrous acid on oleic acid and can be reconverted into it.

In agreement with us, Muller and Shearer as the result of X-ray measurements regard elaidic acid as a *trans* compound. Accordingly the relationship of the two acids is to be expressed by the formulæ:—

$$\begin{array}{l} CH_3 \cdot [CH_2]_7 \cdot CH \\ \qquad\qquad \| \\ \qquad HC \cdot [CH_2]_7 \cdot CO_2H \end{array} \qquad \begin{array}{r} CH_3 \cdot [CH_2]_7 \cdot CH \\ \| \\ CO_2H \cdot [CH_2]_7 \cdot CH \end{array}$$

Elaidic—*trans* acid. Oleic—*cis* acid.

The abundant occurrence of oleic acid is no evidence in itself that it is the most stable form in the chemical sense; rather the contrary, in view of its production as the result of chemical changes induced by enzyme action in the living cell. There is no evidence that elaidic acid is a natural product.

(6) Petroselinic acid, said to be oleic acid-6:7, is obtained from parsley. It melts at 33-34°, and is represented as—

$$CH_3 \cdot [CH_2]_{10} \cdot CH : CH \cdot [CH_2]_4 \cdot CO_2H$$

It also has a stereoisomeric elaidic form.

(7) Cheiranthic acid, m.p. 30°, is very similar to petroselinic acid: its constitution has not been determined.

(To be continued.)

NOTICES OF BOOKS

Spectroscopy, by PROF. E. C. C. BALY, C.B.E., M.Sc., F.R.S. Ed. III., Vol. I. Pp. XI. + 298; figs. 138. London: Longmans, Green & Co., 39, Paternoster Row, E.C.4. 1924. 14s. net.

Prof. Baly's *Spectroscopy* is so well known that it needs neither introduction nor description. The present edition is the edition of 1912 extended both in Age and Area. So extended, in fact, on account of the enormous amount of recent work that the present volume includes but the first half of the original book.

The laws of refraction of light, although discovered by Snell in 1621, were but imperfectly known until the time of Descartes. Some forty years after this, Newton performed his classical experiment and obtained what he termed a "spectrum." Little more was done until Fraunhofer, realising the importance as measuring standards of the black lines discovered by Wollaston in the solar spectrum, mapped some

seven hundred of them; and thus laid the foundations of modern spectroscopy. Similar measurements were afterwards made by Angström, and in 1868 he published his map of the Normal Solar Spectrum, which gave for the first time a standard of reference on a physical basis, by means of which wave-lengths of lines in unknown spectra could be determined. An increasing number of workers now began to carry out research in every direction. Notable amongst these was Rowland, who published a complete photographic map of the solar spectrum, based on his method of ruling and mounting gratings. Subsequently, however, it was shown that the errors of grating measurements were too great for present needs, and therefore grating measurements have had to give place to interference measurements. During recent years the new standard has been agreed upon by the deliberations of International Committees meeting at intervals from 1904 to the present time.

The first two chapters of the book give a historical review of the subject. The next chapter discusses in detail the slit, prisms and lenses of the spectroscope, and further chapters deal with the complete prism spectroscope, the diffraction grating, and their use in practice. These are followed by a chapter on the extreme infra-red and ultra-violet regions of the spectrum which, in view of the widespread interest on all sides in light of short wave-length, will be of particular interest to many, as it contains methods of work on the ultra-violet region. Finally, there is a short but valuable chapter on the practical resolving power of the spectroscope. The theoretical resolving power of a spectroscope refers to an instrument with an infinitely small slit—a condition which cannot be attained in practice. The increase in width of the slit—a condithe resolving power, hence this becomes an important factor.

Spectroscopy, in common with many other subjects originally of purely academic interest, has recently so developed as to become a science in itself of first practical application. The important practical aid it can offer to the working chemist—not merely to the high-brow potential discoverer of new elements—has many times been emphasised.

Here is a first-class practical book, written by an acknowledged authority, and crowned with those final glories of book-blessedness, author and subject indices, crying out the directions in the plainest possible way of the right road to work with the spectroscope. E.H.E.

Atoms and Rays, by Sir Oliver Lodge, F.R.S. Pp. IX. + 208. London: Messrs. E. Benn, Ltd., 8, Bouverie St., E.C.4. 1924. 21s. net.

Any scientific subject which has grown sufficiently to extend into many branches of learning requires close study, and the serious student of to-day must, of necessity, possess himself of several books if he is going to become thoroughly familiar with the subject. The reason is not far to seek, for different authors present the subject with accents, so to speak, on different features.

In this book, Sir Oliver Lodge's treatment is from the point of view of Bohr's theory and the similarity of planetary phenomena as is shown by the following quotation: "Atoms are extremely, almost inconceivably, small; and yet they consist of parts which are millions of times smaller. And recently it has been found, and almost if not completely proved, that the atoms are constructed somewhat on the basis of a solar system; that is to say, that they have at the centre a massive nucleus consisting mainly of an aggregate of protons, with a definite number of electrons circulating round the nucleus, very much as the planets revolve round the sun. And furthermore, that the particles themselves are so small that their distances apart inside the atom are comparable with the distances of the planets from each other and from the sun, in the solar system, in proportion to the size of these bodies.

"But, obviously, a solar system consists mainly of empty space; the part which is really occupied by matter being but a small fraction of the whole. It is manifestly extremely porous. So that any straight line drawn at random through it would be very unlikely to hit one of the planets or even the central sun. Are we to suppose that an atom, too, consists mainly of empty space, and is as porous as a solar system? Yes, that is exactly the idea which the evidence conveys. And it must be regarded as an undoubted fact that an atom, though apparently so solid and impervious and full of material, is really a number of electrical specks, each of utterly imperceptible size, and occupying an insignificant fraction of

the space included within the boundary of the atom: all the rest of which seems empty. If all the electrical particles which compose a human body could be violently compressed into absolute contact, the bulk would be reduced to a billionth part; and sixteen stone would then occupy only a fraction of a cubic millimetre, instead of twenty-two gallons."

The reader will see from the above that the diction leaves nothing to be desired from the point of popular exposition; in short, Sir Oliver Lodge's style is charming. It must not be supposed, however, that the author does not enter into some deep matters involving elementary mathematics. In fact, as simple as the author's style is, there are parts which require to be thought out by the reader. This is not a fault in the book—it is because the subject has gained a firm hold on the analytical brain, owing to certain mathematical calculations affording a wonderful co-ordination of knowledge. It would not be doing the subject justice to omit these cardinal features; and perhaps it is safe to say that the mathematical co-ordination in itself is not as yet fully translated into other safe language, though a good deal of it is.

There are only two criticisms we should like to submit. *First*, that on page 47 the idea is conveyed that Dr. Aston revealed the whole-number isotopes of the common elements as far back as 1913. There must be a misprint here, as it was not until 1919 that Aston's work appeared. *Second*, that the price of the book is too great, considering that the sale will be large, and the cost of production could not have been anything like that of other books containing more diagrams and formulæ, yet published at a lower price.

The book is, without doubt, a most illuminating contribution to the subject, and it will be widely read. Dr. Lodge, as a teacher, has always been held in high esteem.

Examples in Chemistry, by WILLIAM W. MYDDLETON, D.Sc. Pp. VIII. + 134. London: Methuen & Co., 36, Essex St., W.C.2. 1924. Price 3s.

In this volume, examples have been collected for the use of students taking the usual courses in inorganic and general chemistry.

The exercises in each chapter have been devised to test the pupil's knowledge of the fundamental principles of that particular section of the subject.

Among the matters upon which the questions have been based are the separation of mixtures, solubility, the gas and other laws, equivalence, atomic and molecular weights, and chemical equations. More difficult examples have been placed in a separate section, but the advantage of this does not seem to be very great. The answers are given at the end, thus making the book of considerable value to teachers.

Chemical Synthesis, by HARRY HEPWORTH, D.Sc., F.I.C. Pp. XX. + 243. London: Blackie & Son, Ltd., 50, Old Bailey, E.C. 1924. 20s. net.

This volume is one of the series published under the editorship of Prof. R. M. Caven, who points out in an introductory note that organic chemistry, as a science, is not yet a hundred years old—it is still four years to the centenary of Wohler's synthesis of urea. The development of the science during this time has been truly remarkable, especially when it is remembered that many of the early discoveries must have been made under great difficulties. The natural starting materials in the isolation of organic compounds are often so complex and contain bodies of very similar properties, hence they are difficult to separate.

The present volume is concerned with the recent developments of organic chemistry from the opposite direction, viz., the building up of complicated compounds through the agency of plant and animal life.

Recent work in connection with the natural synthesis of organic substances is presented in a clear and comprehensive manner. The author has commenced with a chapter on the photosynthesis of these bodies by the chlorophyll of the green leaves. It is mentioned that many naturally occurring nitrogen compounds have recently been prepared photosynthetically without the intervention of plant life. This has led to the assumption that an activated form of formaldehyde exists under certain conditions.

The extraction of plant pigments such as chlorophyll, carotin and the antihyocyanins is next described in detail. Their formation in the plant tissue is considered, and there is a lengthy chapter on the various

carbohydrates. This is followed by a brief but good account of the depsides, lichen products and the tannins.

Among the other groups of naturally synthesised bodies described are the animal and vegetable oils, fats and waxes; the terpenes; the amino-acids and polypeptides; pyrimidine and purine bases, and the alkaloids.

The book will prove of value to many, especially advanced students.

BOOKS RECEIVED.

The Paper Makers' Directory of All Nations. Pp. LVI. + 983. 1924. Thirty-Third Edition. Messrs. Dean & Son, Ltd., 29, King Street, Covent Garden, W.C.2. 21s. net.

Atoms and Rays, by SIR OLIVER LODGE, F.R.S. Pp. IX. + 208. 1924. Messrs. Ernest Benn, Ltd., 8, Bouverie Street, E.C.4. 21s. net.

Business First Principles, by A. F. SHEPHERD. Pp. 48. 1924. Business Builders, Ltd., Crew House, 26, Gt. Ormond Street, W.C.1. 1s. net.

Numerical Examples in Chemistry, by WILLIAM R. FIELDING, M.A., M.Sc. Pp. 108. 1924. Price 1s. 3d.

New Patents.

THIS list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

Latest Patent Applications.

15461—Eagle Picher Lead Co.—Manufacture of basic lead sulphate. June 26.

15253—Karpen & Bros., S.—Manufacture of hexamethylenetetramine. June 24.

15260—Cassella & Co.—Production of arsinic acids. June 24.

15599—Vains, A. R. de.—Continuous manufacture of hydrate of chlorine. June 28.

15600—Vains, A. R. de.—Continuous chlorination of cellulosic materials. June 28.

Specifications Published this Week.

193057—Berlin, D. W. — Method for reducing metallic oxides.

217468—Wallace, W. M.—Recovery of soda from its solutions.

Abstract Published this Week.

215470—Ammonium sulphite and sulphate.—West, J. H., 33, Inverness Terrace, Bayswater, London, and Jaques, A., 37, Sandringham Road, Waterloo, near Liverpool.

A mixture of ammonium sulphite and sulphate is prepared by introducing ammonia and water vapour or ammonia, water vapour and water in a fine state of subdivision into a mixture of sulphur dioxide and air, the proportions being such that the temperature does not rise above 100° C. and that the product is obtained in a substantially dry condition. Slight excess of water vapour beyond the quantity theoretically required is employed, however, in order to obtain the product in an active condition capable of rapid oxidation wholly to sulphate. The mixture of sulphite and sulphate is exposed to air in heaps which are gently raked mechanically or by other means. Part of the air may be introduced together with the ammonia and water vapour, and the ammonia may be used in slight excess. Most of the ammonium sulphite-sulphate mixture is precipitated on cooling the gaseous reaction mixture to a temperature not exceeding 40° C., but a further quantity is recovered by means of a Cottrell precipitator. A filter consisting of ammonium sulphate supported on perforated trays, may also be employed, and the issuing gases are finally passed into a tower and scrubbed with water, ammonia being recovered from the resulting solution of ammonium salts.

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THE CHEMICAL NEWS,

VOL. CXXIX. No. 3354.

THE ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS.

ANNUAL GENERAL MEETING.

The Eighth Annual General Meeting of the Association was held at the Chemical Society's Rooms, Burlington House, Piccadilly, W.1, on Thursday, July 17, 1924. Sir Max Muspratt, Bart., occupied the chair.

The Chairman, in moving the adoption of the Annual Report, said:—

The Association has again gone through a most successful and important year. We have no changes in the personnel of the Council to record, but there are members of Council who have taken up work in other spheres where their co-operation is very valuable. Our General Manager, not being satisfied with the small scope which the Association affords him, has become the President of the Society of Chemical Industry. Much as the members of the Council felt that it was asking them a great deal to allow their General Manager to devote much of his time to the other important body, we felt that in the interests of co-operation between everyone concerned with chemical industry and chemical science, we ought to grant the permission, and I feel confident that all the members agree with that wise course. (Applause.) Undoubtedly in the past the Society of Chemical Industry and the Association of British Chemical Manufacturers, although their membership in many ways overlapped, were not working in the close operation that was best for the members of the two bodies, and I am extremely pleased to think that under the late President of the Society of Chemical Industry, Dr. Armstrong, and under the presidency of our General Manager, Mr. Woolcock, that co-operation and close working together is going to be enormously improved. I have just come from Liverpool, where the Annual Meeting of the Society of Chemical Industry was held last week, and I believe it was a most successful gathering. The thing that I gathered from it was that the close co-operation between manufacturers and others associated with the chemical industry has made great strides in the recent past, and, I venture to think, with satisfaction and advantage to both bodies it will continue to make even greater strides in the future.

Another method of co-operation between those interested in chemistry has been afforded by the very prominent part that this Association has taken in the British Empire Exhibition. When other industries were standing back and could not make up their minds, the Chemical Industry did decide that they were going cordially to support the Exhibition, and the result, I venture to think, is an exhibit second to none of any given in the world, showing the complete range from the simplest domestic chemical products, through the more refined products, right away up to the pure Scientific section. It is a chemical education or all who go to the Exhibition. Nothing of the kind has been tried before, and no great exhibition in the future, I venture to say, will be complete which does not carry on that idea. The Exhibition not only brings chemical manufacturers and consulting and scientific chemists and others interested together, but it is giving a great message to the whole world. It is showing the position this country occupies in science and chemical industry, and a vast number of students from all parts of the country are flocking to that Exhibition and spending much of their time in the chemical section. Those students will help to form an enlightened public opinion of the next generation, and it is most valuable that chemical industry should thus take its right position. But the response of the general public also has been enormous. Even on a day like Bank Holiday, when one would think that the "Fun Fair" would attract all those who were in the Exhibition grounds, the numbers who visited the chemical portion were very large, and very many bought those sixpenny text-books which were sold in the scientific section, showing how seriously and earnestly the general public are now taking the chemical industry. Then again, the influence upon the world at large, the distinguished men and women who are coming from all parts of the world, the visits of scientists, industrialists, politicians, statesmen and others, means that a large proportion of these are being influenced by what they are seeing at that

Exhibition in which our Section, we venture to say, is one of the most excellent. It has been mooted in high quarters that it may be possible that the Exhibition will be opened again next year and succeeding years. I, for one, cordially welcome the suggestion, and I hope that the chemical industry will again, as it has done this year, support it. I am certain that direct and indirect advantages to the whole industry and the individuals composing it will accrue.

There is a reference in the Report to the films for chemical industry. These films are being shown in quite a number of cinematograph halls throughout the country, and they help to concentrate interest in the chemical industry. Any firm who wishes to give a private exhibition for their working people or people who might be interested in their particular line of business can always obtain the free use of these films just for the cost of the carriage.

On the subject of dyestuffs so much has been said and thought that I do not propose to make any long statement. All I wish to point out is this, that the subject is extremely difficult, and within the Association the interests are very conflicting. The Council of the Association has tried to keep the balance between these various interests and to make representations in the right quarter, not with a view to what is good for this firm or that firm, or for any group of firms, but to what is best for the whole industry. If, at times, we have trodden upon the corns of specific interests, that has got to be done if we are to do our duty by the whole of the members of the Association.

There is just a reference in the Report to the Safeguarding of Industries Act. Unfortunately, that has come into a sphere where political ideas play a larger part than industry; but Part I. is still to continue in operation for some little time to come, and I hope that as far as possible the subject will be kept away from political principle or prejudice—words, I am afraid, at times synonymous.

A question that is coming forward in the near future is the Consolidated Factories Bill. This deserves serious consideration. The Association has not taken a narrow-minded view with regard to such legislation; it has always tried to see the principles which the Board of Trade or the Home Office wished to have enforced in industry. At the same time, it has taken the necessary steps to watch the matter, not with a view to blocking the progress of the principle, but to see that something workable comes out as a result of the discussions which have taken place. We are taking the same course of action in this field as we have taken in others—that is to say, we are approaching the matter with a sympathetic mind, with a desire to live in the present day, not looking upon the practise of the past as anything sacred which must not be touched, we do want to have good conditions for our work people. We want them to live their happiest lives through their time in the factory, but at the same time we venture to think that we know the psychology of our workers a good deal better than any Government officials can do, and we think that some kind of latitude and elasticity should be given in these regulations. There is no object in putting in wash-bowls, for example, when we know perfectly well that they are put in in places where they will never be used. We want to make employment easier and pleasanter in our works, but we do not want to be run into a great deal of unnecessary expenditure which is not going to have any result in the way of happiness for our work people.

In the question of Patent Law, Chemical Industry is largely interested, and seeing that a Trade Marks, Patents and Designs Federation has been formed, the Council has appointed a very excellent representative in the person of Dr. Ree. Next comes the question of assessment for rating.

The rating laws of this country are an absolute quagmire. The thing has grown up with no definite principle as to how rates should be levied, and in this attempt under the Rating of Machinery Bill to deal with one section of the problem, almost every other section has been involved, and every kind of principle (or want of principle) in connection with rating has had to be considered and, if possible, consulted. Personally, I am not very hopeful that very much is coming out of this Rating of Machinery Bill, and we can only hope that the enquiries that are going forward with regard to the whole principle of rating will, in the course of two or three years, cause something to emerge that will put upon Chemical Industry—the members of which, let it be remembered, are citizens—a fair incidence and not an unfair incidence. We do not want to push our burdens upon other people, but on the other hand we do

not want to carry unfair burdens, and I hope that every member who can suggest how such consolidation can be obtained will give us the benefit of his experience.

The Census of Production is shortly to be renewed. I welcome that decision very much indeed. The difficulties in quite a number of chemical industrial problems are due to the fact that nobody knows the condition in which industry stands in this country, and one has to accept any statements that suit the particular point of view that a speaker is elaborating. A Census of Production, properly carried out, in the course of a decade at the outside, will give a mass of definite information which will enormously aid us in all these problems, of unemployment, of health, of taxation and of rating, and I am delighted to think that upon the Committee which is to decide the form that this Census is to take, Mr. Perry has been nominated. It is a great responsibility, but we could not have it in more efficient hands.

Referring to the fact that he was addressing them for the last time as Chairman of Council, Sir Max Muspratt thanked the members of the Council and the staff for the loyalty, the hard work, the initiative and the common sense which they had shown, and which had made it a very easy and delightful duty to be Chairman of the Council.

The Treasurer (Mr. C. A. Hill), in seconding the Report, dealt more particularly with the Balance Sheet of the Association.

In the course of the general discussion, Dr. E. F. Armstrong referred to the question of transport. There were, he said, a very large number of bodies interested in the question of transport charges. All present, both in their capacities as industrialists and as private individuals, knew that the amalgamation of the railways had so far been of doubtful benefit to the public, and he felt that it was most important that an Association like their own should be very watchful of their interests on this point. If the railways took them in detail, they were lost, but they might achieve something by standing together. He thought they could not congratulate themselves too much on their success at Wembley. The idea of having an exhibit at Wembley was undoubtedly their own, and although perhaps the idea of the Scientific Section did not originate in their Council, he asserted that nobody else would have carried it out in the way it has been carried out except the Association.

Dr. Levinstein said he would like to emphasise the great value of the co-operation with the scientific societies to which reference had been made. The success of the scientific exhibit was very largely due to the assistance given by the Royal Society. They had found a most willing and friendly spirit, and were able to mark out a sphere of influence for the Association. As one who knew a great deal about the subject of dyestuffs, he was naturally precluded from making any useful remarks! (Laughter.) He contented himself with endorsing the very diplomatic language of the Report. He thought the Association was going on from strength to strength, and that the Report spoke very favourably for the position of the Chemical Industry in this country.

Sir John Brunner, Bart., referred to the Chemical Engineering Department of University College, London. The Association knew that an experiment was being tried in education—namely, to form what was very sorely needed in chemical work, a means of study for the chemical engineer. It had been a great point of controversy among those who manage chemical works whether it was possible, in the time which is allotted to a student, to make a chemical engineer. Many people thought that if you were to try to perform any such task you would turn out a half-baked engineer and a half-baked chemist, and that it would be very much better to divide your own staff into two, to have a thoroughly well-trained chemist and a thoroughly well-trained engineer. But there were very many places in our far-flung Empire where one could not afford to have a large staff, and it seemed to him that there would be great openings for the men trained in this Chemical Engineering Department. Every man so trained would be able to go abroad and take jobs single-handed as managers of, not exactly chemical works, but works where chemistry is a very essential part in the running of the works—such as a sugar factory.

The Rt. Hon. J. W. Wilson referred to the questions in the Council which require very delicate handling. He believed that the Council in the past year had always endeavoured to work for the general welfare of the Chemical Industry, and he thought that on the whole the results had been satisfactory and the Association had amply justified itself, even apart from Wembley.

Mr. Sadler suggested that the Association should pay its way, and that they should

call up the full 100 per cent. for this next year.

Dr. Ree (Chairman of the Manchester Chamber of Commerce) said that the Association had fulfilled to a great extent the ideals with which it started. In the old days there was a good deal more friendliness between the British and German manufacturers than between the British manufacturers themselves. That condition of things was now completely altered, and very much to the advantage of the industry.

The motion to adopt the Report was then carried unanimously.

The Auditors, Messrs. Feasey and Company, were re-elected.

Mr. Perry seconded, and this was agreed to.

Mr. Parnaby (Chairman of the Committee of Scrutineers) read the results of their scrutiny, and the Chairman declared the elections duly carried out.

Dr. E. F. Armstrong proposed a very hearty vote of thanks to the Chairman, Sir Max Muspratt, which was seconded by Sir John Brunner and carried with acclamation.

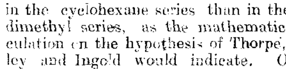
SPIRO COMPOUNDS WITH REFERENCE TO FORMATION AND STABILITY.

Part IV.—Spiro Compounds of Cyclopentane Ketones Derived from Open Chain and Cyclic Glutaric Acids: Derivatives of Cyclohexanespirocyclohexane and of Cyclopentanespirocyclohexane and New Derivatives of Cyclopropane and Cyclohexanespirocyclopropane.

By R. F. Hunter, B.Sc., A.R.C.Sc., M.S.Chim., F.C.S.

This paper is the continuation of the work discussed in this Journal (*loc. cit.*), and the comparison in this case is drawn between $\beta\beta$ dimethylglutaric acid and cyclohexane 1:1 diacetic acid. In Part I., in which the case of cyclohexane 1:1 diacetate was discussed, it was shown that the behaviour of certain derivatives differed notably from the members of the dimethylglutaric acid series. The principal points were concerned with, firstly, the unstable character which the dibromoester of cyclohexane 1:1 diacetic acid possesses owing to the tendency to pass into the brom lactone ester, whereas the corresponding bromo ester in the dimethylglutaric acid series is stable.

Secondly, we were concerned with the great stability of cyclohexane spirocyclopropanedicarboxylic acid, which resists the action of concentrated hydrochloric acid at 240° C., whereas the corresponding dimethyl cyclopropanedicarboxylic acid is transformed into terebic acid by 5 per cent. acid at 200° C. And thirdly, it is desired to emphasise the tendency to the formation of cyclohexylideneacetic acid when the bromo lactone is treated with alkalis. Clearly, then, the fact that groups can be eliminated from the acetic acid residues more readily in the cyclohexanediacetic acid series than in the dimethylglutaric acid series, and further, the fact that the products formed by the establishment of the bond between the residues are more stable in the cyclohexane series, are both in full accord with the idea that the acetic residues are closer together in the cyclohexane series than in the gem dimethyl series, as the mathematical calculation on the hypothesis of Thorpe, Beesley and Ingold would indicate. On the other hand, the relation which the conversion of the bromo lactone ester into cyclohexyledeneacetic acid in large yields under varying conditions bears to the molecular structure is not very clear, although there can be little doubt that it is connected with the greater stability which, according to the hypothesis, would be induced on the semicyclic double bond by the cyclohexane ring when one compares the double bond with that in dimethylacrylic acid. The work of Thorpe and Becker (*J.C.S.*, 1920, 1582) with regard to the cyclopentane compounds showed clearly that as regards stability of the dibromo ester, cyclopentanediacetic acid resembled cyclohexanediacetic acid less closely than it did dimethylglutaric acid. Thus, when ethyl $\alpha\alpha'$ dibromocyclopentane 1:1 diacetate was under reduced pressure, the larger portion passed over unchanged, only about 10 per cent. being converted into the bromo ester (1).



(1)

Under similar conditions the cyclohexanebromoester was completely converted into the bromolactone ester and ethyl bromide. Ethyl dibromodimethylglutarate in

small quantities distils nearly without decomposition, while slow distillation can give a bromolactone ester. The work further showed that cyclopentanespirocyclopropane 1:2 dicarboxylic acid does not possess the same stability as the corresponding cyclohexane derivative. Thus, while the latter is stable to concentrated hydrochloric acid at 240°, the former is rapidly decomposed, even at 200°, with 5 per cent. acid. Under these conditions, the dimethyl analogue is also decomposed. Thirdly, cyclopentylideneacetic acid can be isolated from the product obtained by the hydrolysis of the bromo.lactone ester (1). It is, however, formed in a very much smaller yield than in the case of corresponding cyclohexylidene derivative; in the dimethyl series this reaction is not observed, and this gives some ground for regarding the reaction as being peculiar to cyclic derivatives. In view of these facts, it can be said that the chemistry of the cyclopentanediacetic acid series comes well into line with the experiments which were recorded in the earlier investigations (*loc. cit.* and *J.C.S.*, 1915 and 1919).

Ethyl αα′ dibromocyclopentane 1:1 diacetate is produced by the action of pentabromide of phosphorus on the anhydride of cyclopentane 1:1 diacetic acid, and subsequent treatment with alcohol. From this a good yield of the bromo lactone (1) can be obtained by repeated distillation; this, on hydrolysis with 25 per cent. potash, gives cyclopentylideneacetic acid and the lactonic acid of αα′ dihydroxycyclopentane 1:1 diacetic acid. The similarity between the open chain series and that containing the five-membered ring is also shown by the bromination of the diacetic acids. Thus the bromination of cyclopentane 1:1 diacetic acid leads to the formation of ethyl α bromocyclopentane 1:1 diacetic acid, in the same way as dimethylglutaric acid yields ethyl α bromoglutarate. It is noteworthy that it was not found possible to obtain the alpha brominated ester of cyclohexane 1:1 diacetic acid. In cases of bromination and dibromination, besides the neutral esters obtained, one and the same acid is produced (*J.C.S.*, 1920). The acid product of bromination, as well as the neutral ester, on treatment with concentrated potash solution, yields, in addition to the lactone of α hydroxycyclopentane diacetic acid, both the *cis* and *trans* forms of the spiro acids.

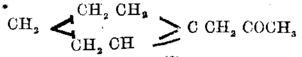
At this point, Kon's work on the ketones derived from open chain and cyclic glutaric acids appears of especial interest (*J.C.S.*, 1921). For the purpose of establishing the modified strain theory it was necessary to employ a careful comparative investigation on the conditions governing the formation of different carbon rings, and with this purpose in view Kon undertook the fourth of this series of investigations on spiro compounds.

A number of methods have been used and recorded for the production of alicyclic systems, but the two of fundamental importance are: the distillation of calcium salts of dibasic acids, and the elimination of alcohol from esters of the acids of the dibasic series. The two methods were of particular interest, since they are both concerned with the conversion of dibasic acids into ring ketones, and further, since they constitute some of the strongest evidence for the Strain theory of von Baeyer, for the only members which undergo ring formation smoothly are the acids of the adipic and pimelic type which produce five and six-membered rings. It is noteworthy that the acids capable of being converted into ketones are incapable of yielding anhydrides. Thus while succinic and glutaric acids readily yield anhydrides, they are not converted into ring ketones and, *vice versa*, pimelic and adipic acids are capable of transformation into ring ketones but incapable of yielding anhydrides. The limiting condition appearing to lie between glutaric and adipic acids. In a paper on the conditions of formation of unsaturated and cyclic compounds from halogenated open chain derivatives, attention was drawn to the fact that the gem dialkyl group has the remarkable effect of promoting the formation of three, four and five-membered rings, which is in agreement with the hypothesis of Ingold, Beesley and Thorpe. Owing to the enhanced stability due to the gem grouping, the gem substituted acids of the glutaric acid series occupy a position which is intermediate between the glutaric and adipic acids in the scale of ketone stability, and it appears probable that they occupy positions in which restricted region anhydride and ketone formation are both possible under suitable conditions. And hence Kon investigated, besides glutaric, β methyl glutaric and ββ dimethylglutaric acid, three cyclic derivatives which had been previously been prepared: cyclopentanediacetic, cyclohexanediacetic, and cycloheptane diacetic acids, with reference to their capa-

city for passing into ring ketones by means of the reactions discussed in this paper, and studied, therefore, the distillation of the calcium salts of the acids. Although the cyclic ketones derived from the different glutaric acids in no case survived the reaction, it was possible to recognise their formation owing to the simple character of the decomposition products subsequent to formation. Whereas with glutaric and β methylglutaric acid there was obtained no evidence of the production of four-membered ring ketones, yet in every case in which the gem acid was used, that is, in the cases of $\beta\beta$ dimethyl, $\beta\beta$ diethyl glutaric acid and cyclopentane, hexane and heptanediacetic acids, the formation of a ring ketone was the primary reaction. Few investigations on the thermal decomposition of highly strained rings had been carried out previous to Kon's work, but those which had been carried out showed that the primary products were always due to isomerisation to an open chain isomeride. Thus, cyclopropane at red heat isomerises to propylene (*Ber.*, 1896, XXIX., 1,297, and 1899, XXXII., 702), and it has been shown that in the presence of contact material below 400° C. methylcyclopropane and 1:1 dimethylcyclopropane undergo similar transformations. It is not remarkable, therefore, that Dr. Kon found that the cyclic ketones produced during distillation, in all the cases in which there was a primary product isomerised to the open chain unsaturated ketones. Thus the cyclic ketone from dimethylglutaric acid yields mesityl oxide, and that from cyclohexane diacetic acid is transformed into Wallach's ketone. In the same way, cyclopentanediacetic acid gives cyclopentenylacetone; cycloheptane diacetic acid gives cycloheptenylacetone.

No trace of the corresponding unsaturated ketones could he isolated from the distillates of glutaric methylglutaric acids, however. With regard to the unsaturated ketones obtained from $\beta\beta$ substituted glutaric acids, exhaustive examination of the distillates revealed three decomposition products, evidently derived from the unsaturated substances by the hydrolytic action of water which was always present under the experimental conditions. Thus from dimethylglutaric acid there was obtained acetone, isophorone and β methylpropylene. Similar products were isolated in the other cases.

It was clear that valuable evidence regarding the conditions of stability of spiro compounds would be obtained by an examination of the hydrocarbons themselves; say, for example, cyclohexanespirocyclohexane and cyclopentanespirocyclohexane, and it was obvious that the best way to prepare the hydrocarbons was by the method by which Vorlander had obtained dimethyldihydroresorcinolcarboxylic ester, by the action of ethyl sodiomalonate on mesityl oxide, because not only is this reaction a smooth one, but the method for preparing hydrocarbons had been worked out by Crossley and his collaborators. At first sight it did not seem as though it would be an easy matter to obtain the compounds analogous to dimethyldihydroresorcinolcarboxylic ester and which were to form the basis for the investigation, because the only ketones allied to mesityl oxide in the cyclic series which had hitherto been prepared were cyclohexenylacetone (2) and cyclopentenylacetone (3).



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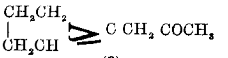


(3)

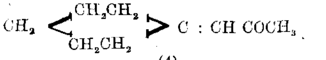
Wallach's ketone (2) was prepared by the condensation of cyclohexanone and acetone, and also by Kon, as indicated above, and there could be no doubt as to the substances since they gave identical semicarbazones and had the same refractive index. It is clear that the absence of exaltation was what led Wallach to place the double bond in the ring of his compound, and a similar formula was therefore assigned to the ketone (3) by Dr. Kon, which he obtained by the distillation of the calcium salt of cyclopentanediacetic acid.

It did not seem likely, therefore, that, assuming the physical evidence of structure to be correct, the desired condensation product could hardly be obtained from these ketones, for one reason: Perkin and Harding showed that in the case of the similarly constituted cyclohexenylacetic ester no condensation product is formed with ethyl sodiocyanoacetate, and, in fact, that the rule regarding the inability of $\beta\gamma$ unsaturated ketones to undergo the Michael con-

densation is strictly adhered to. Nevertheless, it was decided to condense (2) and (3) with ethyl sodiomalonate, to find whether it was possible to cause the interaction to ensue under special conditions. It was remarkable to find, therefore, that under the conditions described by Vorlander, an 80 per cent. yield of condensation product was obtained.

These compounds, in the hydrated form in which they were always isolated by Thorpe and Norris, were crystalline solids which, on hydrolysis, passed into the dihydroresorcinol derivatives. It was not considered on chemical evidence that there was any need to doubt the structures which had been assigned to the ketones (2) and (3) by Wallach and Kon were incorrect. With the object of strengthening this and finding evidence in favour of the structures (4) and (5), the negative evidence of Perkin and his collaborators was extended by Thorpe and Norris.

By condensing cyclohexylideneacetic ester with ethyl sodiocyanoacetate, a cyano ester was obtained which had been obtained previously from cyclohexanediacetic acid on hydrolysis. This, then, appears to be definite proof that the beta gamma ester did not undergo the Michael condensation, and that the alpha beta ester did so.



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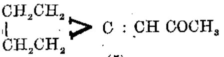

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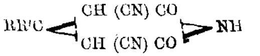
The constitutions of the spiro compounds were confirmed by oxidation; cyclohexanespirocyclohexane 3:5 dione gave cyclohexane 1:1 diacetic acid on oxidation with hypobromite, and cyclohexanelacetic 1 carboxylic acid with permanganate. In the same way cyclopentanespirocyclohexane 3:5 dione gave with hypobromite cyclopentane 1:1 diacetic acid, and with permanganate cyclopentane 1 acetic 1 carboxylic acid.

How the results of the researches on spirocyclopropane and its derivatives made it desirable to extend the knowledge of their methods of formation, and a perusal of the literature revealed a possible source of cyclopropane derivatives in the bridged piperidine compounds of Guareschi (*Mem. R. Acad. Sci.*, Turin, 1901, and *Atti. R. Acad.*, Turin, 1898 and 1899). The compounds are formed in quantitative yield when imides of the type (6) obtained by the condensation of ketones with ethyl cyanoacetate and ammonia are brominated, and the resulting dibromo compounds (7) subjected to the action of heat or treated with some agent capable of eliminating bromine, the structure (8) was assigned to the compounds.



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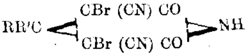

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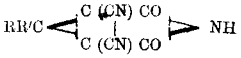


(8)

At first sight the constitution seems unlikely, owing to the ease with which bridging takes place, and this is seldom observed in cyclopropane compounds. It was decided to investigate the matter further, and to endeavour if Guareschi was correct to use the compounds as a source of cyclopropane derivatives. Two typical examples were investigated, the dimethyl compound in which RR′ = 2Me, and the cyclohexane compound in which RR′ = C_5H_{10}, which, if the formulæ were correct, would be capable of conversion into caronic acid and cyclohexanespirocyclopropanedicarboxylic acid. It was clearly demonstrated that the cyclohexane compound was more stable, which points to the cyclohexane ring conferring stability on the cyclopropane ring, having a spirane carbon atom common to both. It was highly important to establish the constitution of the bridged imides, but it was difficult, owing to the variety of products obtainable by the use of numerous reagents. Thorpe and his collaborators, however, finally showed the constitution to be (8). It was found that acid hydrolysing agents caused deep-seated changes, but that the regulated hydrolysis

with alkali led to the formation of a variety of products, according to the conditions of the experiment. It was found that the cyclohexane compound was somewhat more readily hydrolysed than the dimethyl compound. If boiled for ten minutes with a molecular proportion of 10 per cent. potash, the imino ring is broken, and at the same time the expulsion of a molecule of carbon dioxide takes place with the formation of the amide in quantitative yield. An analogous compound was obtained from the dimethyl compound, the only difference being that a certain amount of material was always recovered unchanged. On further hydrolysis with alkalis these compounds undergo fission.

The dicyano acids can be prepared directly from the imides by the action on the latter of two molecules of KOH in dilute solution. Although the amides are unaffected by heating with water under pressure at 180° C., the corresponding imides are converted into nitriles with loss of carbon dioxide under these circumstances; the nitriles are capable of hydrolysis to dicarboxylic acids with alcoholic potash. It is noteworthy that no fission occurs; although the action of potash on amides, no doubt owing to the presence of two quaternary carbon atoms, leads to the rupture of the cyclopropane ring and the formation of lactonic acids.

Evidence which bears on the stability of the compounds was obtained by the study of the behaviour of the two bridged imides with three or more molecules of alkali. In the first place, the two compounds were subjected to the action of concentrated alkali at high temperature. The main product when the cyclohexane compound is used is the lactonic acid, but an appreciable amount of spiro acid is also formed. Not a trace of caronic acid could be isolated, however, from the dimethyl compound, and here it must be concluded that the cyclopropane ring is too unstable to survive the conditions of experiment. The most illuminating facts, however, were afforded by the hydrolysis of the original imides by means of three molecules of potash in aqueous solution. Under these conditions the cyclohexane compound gave a dicyano dicarboxylic acid in nearly quantitative yield, while the dimethyl imide gave an analogous acid in good yield, but with the constitution + a molecule of water.

The facts in general confirm the hypothesis of Thorpe, Beesley and Ingold.

Highbury New Park, N.5.
June, 1924.

CYANIDE COMBINATIONS WITH METHYL.

By JOHN MISSENDEN.

The majority of the investigations which have been conducted with respect to this series have been published, strangely enough, in Continental journals. There are several discrepancies with regard to the nomenclature of the series, and cross reference should be made very largely to the carbimides, nitrates, and carbylamines. From time to time considerable doubt has arisen with regard to the authenticity of these various papers, and the reports of a large number of the authorities certainly differ widely. Extensive reference, together with private investigations of a more or less complete character, seem to have furnished acceptable results, although the experiments are by no means complete for the whole of the series.

The first compound of importance is *acetonitrite* (also known as *methyl cyanide*), $CH_3.CN$. A method of preparation has been reported by Henry (*Annalen*, CLII., 149), who distilled five parts of acetamide and one part of phosphorus pentasulphide, afterwards washing with caustic soda and reacting with lead oxide. Dumas (*Comptes rendus*, XXV., 383; *Annalen*, LVIV., 333) investigated several means of production also. The two most noteworthy are the distillation of potassium cyanide with potassium methyl sulphate; and by the reduction of phosphorus pentoxide with ammonia acetate or acetamide.

Acetonitrite is a volatile liquid, perfectly colourless, and with a specific gravity of 0.8054 at zero and 0.7889 at 14° C. Its boiling point is 81.5° C. Upon inter-action with sodium a viscid liquid which is soluble in ether and has a formula $C_4H_6N_2$, is produced, as well as small quantities of *cyanmethine*, $C_6H_9N_3$. A very good method of preparation has been described by Meyer (*Journ. pr. Chem.*, XXVII [ii.], 153), who heated one part of sodium with six parts of methyl cyanide under a pressure of several atmospheres, finally obtaining monoclinic

crystals from alcohol. Ether would serve equally well as a solvent. Cyanmethine forms chlorine and bromine derivatives, and also unites molecularly with many mineral acids, nitric acid being a case in point.

Acetonitrite combines directly with bromine under the influence of heat, with the formation of a crystalline compound having a formula, $CH_3.CN.2HBr$. Another nameless compound is produced in action with sulphur trioxide; this compound is also crystalline and soluble in water. It has a formula $(CH_3.CN)_3.2SO_3$. A further crystalline compound is formed by precipitating with alcohol. This last compound is a monohydrated variety of the former, except that the sulphur group is duplicated.

Iso-acetonitrite is another variety of the compound, and has been designated methyl carbylamine and methyl *iso*-cyanide; it has the formula, $CH_3.NC$. Hoffmann (*Berichte*, 1881, 2,609) effected its synthesis by the interaction of alcoholic potash with methylamine and chloroform. It may also be formed by the distillation of a mixture of potassium cyanide and potassium methylsulphate in combination with the ordinary acetonitrite. A very wide range of crystalline salts can be obtained from most of the acids, and they are distinctive by their extremely repugnant odours. Its specific gravity is 0.755 at 10° C., and its boiling point is 59.2° C.

The next compound is methyl carbimide, also known as *methyl iso-cyanate*, which has the formula, $CH_3.N:CO$. Wurtz (*Ann. Chim.*, XLII. [iii.], 43) produced this compound by distilling two parts of potassium methyl sulphate with one part of potassium cyanate. The two derivatives of the compound are the methyl-urea and the dimethyl-urea, the respective formulæ being $NH.(CH_3)CO \cdot HN_2$ and $NH.(CH_3)CO \cdot NH.CH_3$. The first is obtained by reaction with anhydrous ammonia, and the second is obtained from the first by the addition of water.

There are eight substitution products of acetonitrite which may be divided into two main groups; firstly, there is the nitrate substitution products, and secondly the halogen group. Of the first there is the nitro-acetonitrile, which is better known under the name of fulminic acid. This can be further extended to the dinitro-product and the trinitro-product. The dinitro-product is obtained by subjecting the compound $CH.(NO_2)_2.CH \cdot NH_2$ to the action of sulphuric acid. The compound, which has been expressed by the formula, is obtained according to the following equation: —

$$C(NO_2)_3.CN+4H_2S \rightarrow CH.(NO_2)_2.CN.NH_2 +4S+2H_2O.$$

The trinitro compound is a very violent explosive, and is obtained by subjecting sodium fulminate to the combined action of concentrated sulphuric acid and fuming nitric acid. It is easily decomposed by alcohol.

Of the halogen group there are three chlorine products, mono-, di- and tri-, which have already been described by Scholl, Bisschopinck and Beckart (*Berichte*, VI., 732; *ibid.*, 1896, 2,417; *ibid.*, 1876, 1,594). The bromine products, mono- and di-, have been described by Engler (*Annalen*, CXLII., 69), while the iodine compound, produced from alcohol, sodium, iodide and chloracetonitrile, has been investigated by Henry (*Comptes rendus*, CIII., 413).

A series of cyanurates also belong to this group, and will form the basis of another contribution at an early date.

GENERAL NOTES.

MEDICAL CONGRESS AND EXHIBITION AT SEVILLE.

The Acting British Consul at Seville has forwarded to the Department of Overseas Trade a copy of the programme of the Second National Congress of Medicine, to be held at Seville from October 15 to November 5 next, and a copy of the regulations for the Medical and Hygienic Exhibition to be held during the Congress.

The exhibition is open to exhibitors of all nationalities, but the Congress is limited to medical men authorised to practice in Spain, Portugal, and South America.

The programme of the Congress (in Spanish) and a translation of the regulations for the Exhibition may be consulted at the Department, 35, Old Queen Street, Westminster, London, S.W.1. (Reference, B.X. 1109.)

INFORMATION BUREAUX AND SPECIAL LIBRARIES.

A conference will be held at High Leigh, Hoddesdon, Herts., during the week-end

September 5-8, to which are invited all men and women who need to utilise information systematically, or who are interested in the conduct or operation of information bureaux, intelligence services and special libraries.

The programme will include papers and discussions on the functions, future developments, and the methods and equipment of intelligence bureaux, and on their relations with other institutions, including national and public libraries. It is hoped to obtain representatives of such varied fields of activity as government and municipal departments, technical and research institutions, industrial concerns, financial houses, insurance offices, newspapers, and civic and social organisations, all of which have a common interest in the collection, treatment and dissemination of facts and information relevant to their particular activities.

Further information may be obtained from Mr. A. F. Ridley, Athenæum Chambers, 71, Temple Row, Birmingham.

GARNETS NOW BEING MINED IN CANADA.

The garnet is usually looked upon as a precious stone, but the quantity used as gems is very small in comparison with its use as an abrasive. Some of our most beautiful gems are merely pure forms of comparatively common minerals that are used for abrasive purposes, and it is an interesting fact that corundum, or emery, is known as either ruby or sapphire when transparent and coloured red or blue by certain chemicals.

In recent years the use of all kinds of abrasive materials, both natural and artificial, has greatly increased, and there are now very few articles that we see around us, in factory or home, other than textiles, that have not been subjected in some way or other to the action of abrasives. On account of this increase in demand, the Mines Branch of the Department of Mines, Ottawa, is making special investigations of Canadian abrasive minerals, including garnet.

Garnet is really a very common mineral, and occurs in several varieties, having slightly different composition and colour, and varying considerably in hardness, toughness, and method of breaking. For abrasive purposes the mineral should be very hard—harder than quartz or sand; it should break into sharp angular fragments without curves, or rounded edges, so that it will easily cut or abrade the articles under treatment; and it should have high capillary attraction, so that it will absorb the glue. The variety of garnet that is suitable is usually a heavy mineral of a red-brown colour. Approximately 95 per cent. of the garnet mined throughout the world is used on paper or cloth, and the term "sand paper" is often applied, generally, to papers coated with sand, emery, corundum, or garnet. The last of these has, to a certain extent, superseded the others, since it has wider scope. Garnet paper can readily be distinguished from the others by its pale red colour.

In the manufacture of these papers, the clean garnet is first crushed and graded by screening into different sizes, and is then mechanically fed on to suitably glued, slowly revolving rolls of paper or cloth, which are then re-coated with glue and dried. There are two Canadian firms making abrasive papers and cloths, one at Victoria, B.C., and one at Brantford, Ont. The western concern has, until recently, obtained its supply of garnets from a deposit at the mouth of Stikine river, Alaska, U.S.A.

Very little is yet known about the existence of commercial deposits of abrasive garnet in Canada. In Ontario, the Bancroft Mining Syndicate has been producing a good type of garnet from a rich vein near Bancroft, and a promising deposit of larger extent but lower garnet content, at Parry Sound, has been well prospected, and will probably become an economic producer. Near Sudbury, Ont., there is another promising exposure about 50 feet wide and traceable for a considerable distance. The centre of the deposit contains well-formed garnets, two or more inches in diameter, which gradually decrease to the size of a pin's head as the contacts are approached.

At Chegoggin Point, near Yarmouth, Nova Scotia, a 35 foot dyke with a garnet content of approximately 40 per cent., outcrops on the sea shore, and has been traced inland for several miles. All the above deposits are near rail or water transportation, and should be of commercial importance. Several other deposits are known that are both rich and suitable for abrasive purposes, but they are at present remote from transportation facilities.

It should be borne in mind, however, that the market is limited, and that concentration and preparation for market are important factors. In this connection the Ore Dressing Division of the Mines Branch has recently paid considerable attention to the preparation of Canadian garnets for the market, and has made a number of tests to determine the best processes for different classes of ore.

In America, the price of garnet varies from $80.00 to $50.00 per ton, according to quality and size of grain.

There have recently been enquiries from England for Canadian garnet, and if there is a steady demand, many new deposits of suitable material will probably be found, as there are large areas in which the geological formations give promise of their probable occurrence. Meanwhile it is important that those commercially interested in the mineral should realise that there are known deposits of good quality abrasive garnet in Canada, and that they are being exploited.

There is an exhibit of garnets and of garnet paper at the Canadian Pavilion, Wembley.

The Automatic and Electric Furnaces, Ltd., have issued a new leaflet dealing with oven furnaces with the heaters inside the chamber exposed but yet protected.

The firm of Yannopoulos-Cassaris, of Alexandria, Egypt, are anxious to get in touch with a firm that will supply 20-25 tons of iron sulphate, 5-10 tons each of potassium bichromate, sodium silicate, sodium carbonate, and caustic soda.

The National Association of Master Bakers, Confectioners and Caterers has issued its report on research at the National Bakery School. The work has been conducted by Dr. C. Dorée and Mr. J Kirkland. The reports deal with the variation of weight of loaves due to loss in baking, the weight conserving effects of wrapping loaves in waxed paper, variableness of oven temperatures, and the quicker ripening of hard flour doughs.

CHEMICAL SOCIETY'S LIBRARY.

The Library of the Chemical Society will be closed for stocktaking from August 4 to August 16, inclusive, and will close each evening at 5 o'clock from August 18 to September 18

PROCEEDINGS AND NOTICES OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.

(*Continued from Page* 58.)

Erucic acid, $C_{22}H_{42}O_2$.—This occurs as a glyceride in cruciferous oils, etc.: it has been usually regarded as a *trans* acid, but we prefer to assign this structure to the isomeric brassidic acid, and in this view we have again the support of Muller and Shearer. The acids accordingly have the subjoined formulæ, the ethenoid bond being between carbons 13 and 14, that is the same distance from the CH_3 group as in oleic acid.

$$\begin{matrix} CH_3\cdot[CH_2]_7 \\ H \end{matrix}\Big\rangle C = C \Big\langle \begin{matrix} [CH_2]_{11}\cdot CO_2H \\ H \end{matrix}$$

Erucic acid.

$$\begin{matrix} CH_3\cdot[CH_2]_7 \\ H \end{matrix}\Big\rangle C = C \Big\langle \begin{matrix} H \\ [CH_2]_{11}\cdot CO_2H \end{matrix}$$

Brassidic acid.

Unsaturated acids, $C_nH_{2n-4}O_2$.

Linoleic (*linolic*) *acid*, $C_{18}H_{32}O_2$.—Great confusion is introduced into attempts to determine the structural formulæ of this group of acids, owing to there being four geometrical isomerides possible of each substance. Probably more than one linoleic acid occurs in the animal and vegetable fats, but whether the isomerism is structural or geometrical cannot be stated.

The accepted formula for linoleic acid is:

$$CH_3\cdot[CH_2]_4\cdot\underset{13}{CH}:\underset{12}{CH}\cdot CH_2\cdot\underset{10}{CH}:\underset{9}{CH}\cdot$$
$$[CH_2]_7.CO_2H.$$

The acids of Chinese and Japanese wood oil, variously named elæostearic and elæomargaric acid, are characterised in particular by the readiness with which they undergo oxidation. This suggests another arrangement of the ethenoid bonds in them, and the latest constitutional formula suggested is:

$$CH_3\cdot[CH_2]_3\cdot\underset{14}{CH}:\underset{13}{CH}\cdot CH_2\cdot CH_2\cdot\underset{10}{CH}:$$
$$\underset{9}{CH}\cdot[CH_2]_7\cdot CO_2H.$$

Unsaturated acids $CnH_{2}n-_{6}O_{2}$.

Linolenic acid with three unsaturated ethenoid linkages offers opportunity to still greater isomerism and confusion. The formula suggested by Erdmann and Goldsobel has the double bonds between carbons 9 and 10, 12 and 13, 15 and 16. Salway assumes the presence of a grouping:—

$$\underset{14}{-CH} : \underset{13}{CH}\cdot\underset{12}{CH} : \underset{11}{CH}\cdot\underset{10}{CH} : \underset{9}{CH-}$$

but this conflicts with the formula agreed for linoleic acid. This field invites further investigation, but much has to be done first to characterise the unsaturated acids and their decomposition products.

The more unsaturated acids have not been isolated: they occur in the oils derived from marine animals as evidenced in the analyses in Table III.

Acids $C_{2}H_{2}n-_{2}O_{3}$.

Ricinoleic acid, $C_{18}H_{34}O_{3}$, is the acidic constituent of the principal glyceride of castor oil. It has the ethenoid bond as in oleic acid between carbons 9 and 10 and the hydroxyl group on carbon 12 as expressed by the formula:—

$$\begin{array}{l} CH_{3} : [CH_{2}]_{5} : CH(OH) : CH_{2} : CH \\ \qquad\qquad\qquad\qquad\qquad\qquad \| \\ \qquad\qquad\qquad\qquad\qquad HC : [CH_{2}]_{7} : CO_{2}H. \end{array}$$

It thus occupies an intermediate position between oleic and linoleic acids, if it be supposed that the hydroxy compound precedes ethenoid bond formation.

It is optically active; nitrous fumes convert it into the stereoisomeric ricinelaidic acid.

It remains only to mention the closed-chain acids of the chaulmoogric series, which are isomeric with linoleic acid, but contain only one ethenoid bond.

Mixed glycerides.

Our knowledge of the processes of nature enables it to be stated that in all cases selective action is at work choosing one form of a substance out of many for further elaboration. Materials, whether they be proteins or carbohydrate derivatives, etc., are made to a definite geometrical pattern almost as if they were laid down against an existing template. The fats in nature form no exception to this rule, the fatty acids being stored in the form of mixed glycerides which are asymmetric and differ from one another in the location of a particular fatty acid radical in the glycerol molecule.

A diglyceride may thus be either:—

$$C_{3}H_{5}\begin{cases} OR_{1} \\ OR_{2} \\ OR_{2} \end{cases} \quad \text{or} \quad C_{3}H_{5}\begin{cases} OR_{2} \\ OR_{1} \\ OR_{2} \end{cases}$$

whilst for a triglyceride there are three alternatives:—

$$C_{3}H_{5}\begin{cases} OR_{1} \\ OR_{2} \\ OR_{3} \end{cases} \qquad C_{3}H_{5}\begin{cases} OR_{2} \\ OR_{1} \\ OR_{3} \end{cases} \qquad C_{3}H_{5}\begin{cases} OR_{1} \\ OR_{3} \\ OR_{2} \end{cases}$$

Glycerides, as is well known, are hydrolysed by an enzyme named lipase, but we have no knowledge as to how a given preparation of lipase would behave towards the three isomeric triglycerides represented above. They might be hydrolysed at the same rate, at different rates or in stages. In order that such questions can be answered, it appears eminently desirable that all these compounds should be prepared and their properties studied.

We are able to report some experiments by C. W. Moore on the *saponification* of fatty acid esters and glycerides with alcoholic potassium hydroxide. He finds that the primary esters of the higher fatty acids are hydrolysed at the same rate in equimolecular concentration, and concludes that the α-monoglycerides of the acids would also be hydrolysed at the same rate. He was unable to prepare β-monolaurin to compare its behaviour with the α-isomeride owing to internal rearrangement in the molecule taking place, but he was able to show that trilaurin and monolaurin are changed at the same rate and that the hydrolysis does not take place in stages.

It is probable, indeed, that the action of lipase is not affected by the nature of the fatty acid radical except in so far as this may have a secondary influence in affecting the nature of the emulsion between enzyme and glyceride.

(*To be continued.*)

NOTICES OF BOOKS.

Electrode Reaction and Equilibria, A GENERAL DISCUSSION. Pp. 668 to 838. *November*, 1923. *The Faraday Society*. 10s. 6d.

This new number of the unrivalled series of the Faraday Society's "General Discussions" deals with the most fundamental electro-chemical problems, discussing the question, how the electrode potential is acquired, defining the influence of equilibria in solution upon the E.M.F. of galvanic cells, and investigating processes during electrolysis.

Such important phenomena necessitate, of course, wide and manifold descriptions, as is seen from the seventeen communications presented at the Discussion, which had to be divided into two parts, the first concerning "Conditions of Equilibrium at Reversible Electrodes," the second "Irreversible Phenomena of Electrolysis."

In the introductory address of Part I., E. K. RIDEAL summarises the various attempts proposed to explain the origin of the electrode potential, the nature of the "electric double-layer," and the factors of Nernst's "solution pressure"; similar topics are further treated in the papers of J. A. V. BUTLER. In all such considerations the primary process which charges electrodes is sought in the separation of metallic ions from electrons of the electrode, this bringing electro-chemical problems within the domain of physics, mainly electronics of metals. No doubt the present state of this branch of physics is so far advanced as to allow a satisfactory solvation of the more than a century old "Volta effect" problem, yet a certain lack of thermodynamic rigour and a good deal of misunderstanding amongst the workers of different lines of attack has not yet allowed a definitely acceptable formulation.

Closely associated with these problems is the question of the "zero-potential," which is discussed in A. W. PORTER and E. BAUER's communication.

A great simplification in the technic of the determination of hydrions and of the oxidation and reduction potentials in organic chemistry brings the E. BIILMANN'S communication on his well-known quinhydrone electrode. This innovation not only enables one to measure the acidity in the presence of nitrates, but it allows exact affinity measurements of organic bodies. In the paper of J. A. PRING affinity constants of bases are already derived from measurements with the E. BIILMANN electrode.

Another innovation for the study of reversible electrode reactions and ionic equilibria is the use of a slowly dropping mercury cathode, which furnishes an almost currentless and therefore reversible electrolysis. J. HEYROVSKY describes these investigations, pointing out the possibility to develop the method into a qualitative and quantitative electro-analysis.

A paper on similar experiments carried out in alcoholic solutions is communicated by M. SHIKATA, who, in alcoholic concentration cells, encounters a first instance of a very pronounced abnormal increase of activity of sodium ions.

The first part of the Discussion concludes the paper of A. K. GOARD and E. K. RIDEAL, who describe an interesting attempt to change the "irreversible" oxygen electrode into one working reversibly.

This brings the reader to Part II. of the Discussion, where the H. J. T. ELLINGHAM and A. J. ALLMAND's introductory address on "Irreversible Electrode Phenomena" gives an admirably clear systematic account of the present aspect of electrolysis.

It is followed by a paper of A. SMITH, who further develops his well-known ideas on passivity and activity of electrodes. The cause of passivity is further dealt with particularly in U. R. EVANS' communication, discussing this phenomenon from the viewpoint of obstructive film formation.

The rest of the papers (by J. HEYROVSKY, N. V. S. KNIBBS, S. GLASSTONE, R. T. LATTEY) concern the very interesting but not yet quite settled question of hydrogen overpotential. This was also the chief topic of the Discussion, which concludes the publication. Here objections were raised against the commutator method for overpotential determinations, and "transfer-resistance" effects were agreed upon to be of minor importance; the majority of the speakers share the opinion that overpotential is due not to the formation of a gaseous film of hydrogen, but to the very base nature of the alloy which the deposited atomic hydrogen forms with the electrode material.

Not only does the new publication represent up-to-date theoretical electro-chemistry, but, moreover—in accordance with the aims of the Faraday Society's distinguished leaders—it cannot fail stimulating minds to hasten the solutions of the many important and purely scientific problems.

J.H.

BOOKS RECEIVED.

Kolloidchemie und Biologie, von PROF. DR. HERBERT FREUNDLICH. Pp. 47. 1924. Verlag von Theodor Steinkopff, Residenzstrasse 12b, Leipzig, Germany. $0.50.

Skinner's Cotton Trade Directory, by THOMAS SKINNER & CO. Pp. LXXX. + 1328. 1924. Thomas Gresham & Co., Gresham House, E.C.2. 25s. net.

The Carbohydrates and The Glucosides, by E. FRANKLAND ARMSTRONG, D.Sc., PH.D., &c. Pp. VIII. + 293. 1924. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 16s. net.

The Vacuum, by J. A. COCHRANE, B.Sc. Pp. VI. + 103. 1924. Messrs. G. Bell & Sons, Ltd., York House, Portugal Street, W.C.2. 1s. 6d.

The Theory of Relativity—Studies and Contributions, by ARCHIBALD HENDERSON, ALLAN WILSON HOBBS, and JOHN WAYNE LASLEY, JUN. Pp. IX. + 99. 1924. Oxford University Press, Amen House, Warwick Square, E.C.4. 11s. 6d. net.

Licht und Farbe in Kolloiden, von PROF. DR. WOLFGANG OSTWALD, Universitat Leipzig. Pp. XIV. + 556. 1924. Verlag von Theodor Steinkopff, Residenzstrasse 12b, Dresden, Blasewitz, Germany.

Nitroglycerin und Nitroglycerinsprengstoffe (Dynamite), von PROFESSOR DR. NAORIM. Pp. XI. + 416. 1924. Berlin: Julius Springer. 4 dollars 30 cents.

Chemische Reaktionen in Gallerten, von DR. RAPHAEL ED. LIESEGANG, Frankfurt A. M. Pp. 90. 1924. Verlag von Theodor Steinkopff, Residenzstrasse 12b, Leipzig, Germany. 85 cents.

The Kinetic Theory of Gases, by EUGENE BLOCH, Translated by PHILIP A. SMITH, B.A. (OXON.). Pp. XI. + 178. 1924. Messrs. Methuen & Co., 36, Essex Street, W.C.2. 7s.

New Patents.

THIS list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

Latest Patent Applications.

15812—Cassella & Co., Ges. L.—Manufacture of azotriphenylmethane dyes. July 1.

16106—Knoll & Co., Chemische Fabrik.—Manufacture of medicinal jujubes. July 4.

15669—Maxted, E.B.—Oxidation of aromatic hydrocarbons. June 30.

Specifications Published this Week.

217614—Nolan, T. J., Clapham, H. W., and Nobel's Explosives Co., Ltd.—Production of tetryl and ethyl tetryl.

217715—Cassella & Co., Ges. L.—Manufacture of alkyloxyacridines.

217753—Durand & Huguenin Soc. Anon.—Manufacture of chlorinated amines.

217768—Boving, C. M.—Combustible cartridge for the developing of sulphur dioxide.

Abstract Published this Week.

215813—Phosphoric Acid.—Laporte, Ltd., B., and Alcock, H. E., The Knoll, both in Luton, Bedfordshire.

Pure phosphoric acid is produced by decomposing by means of sulphuric acid barium phosphate obtained by the treatment of di- or tri-sodium phosphate with barium sulphide. In an example, to a solution of barium sulphide crystallised di-sodium phosphate and a solution of caustic soda are added until no further precipitation occurs. After filtering and washing free from sodium sulphide, which may be recovered, the precipitate of barium phosphate is decomposed by means of sulphuric acid and the barium sulphate removed. In another example sodium phosphate is formed by treating commercial phosphoric acid with sodium carbonate and caustic soda. Barium phosphate is then precipitated by means of barium sulphide and treated as in the first example. Potassium and ammonium phosphates may be used in place of sodium phosphates.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s 6d. each.

THE CHEMICAL NEWS,

VOL. CXXIX. No. 3356.

OVERVOLTAGE AND PHYSICAL PROPERTIES.

By J. R. Partington, D.Sc.

In the communication on the above subject, in *The Chemical News* for July 11 (this vol., p. 17), Dr. E. J. Weeks gives a table which is intended to show that the higher the melting point of a metal the lower its hydrogen overvoltage in acid solution. Unfortunately, the melting points, as selected by Dr. Weeks, do not correspond with those generally accepted, and when the correct values are substituted for those given in his table, the agreement is modified. The difference is most marked in the cases of tungsten and rhodium, for the melting points of which Dr. Weeks adopts the values 2800° C. and "over 3000° C." respectively. The generally adopted values are 3400° and 1950° respectively. These figures vitiate his conclusion that "the lowest overvoltage is that of rhodium, 0.00, whose melting point is somewhere over 3000° C." As a matter of fact, rhodium comes before tungsten, which has the highest melting point but has at the same time the appreciable overvoltage of 0.35, the highest of all those of metals of higher melting point given in Dr. Weeks's table. The melting points of cobalt (1530°) and iron (1600°) given by Dr. Weeks also differ considerably from those accepted (1480° and 1530° respectively). The arrangement of the metals in the order of melting points as given below shows that, although there is some general agreement, there is no question of any approximately exact relation of the kind postulated by Dr. Weeks.

Metal.	Melting point.	Overvoltage.
Mercury	-39° C.	0.89
Bismuth	271° C.	0.50
Thallium	302° C.	0.54
Cadmium	321° C.	0.50
Lead	327.4° C.	0.61
Zinc	419.4° C.	0.60
Antimony	630° C.	0.54
Silver	960.5° C.	0.23
Gold	1063° C.	0.31
Copper	1083° C.	0.31
Nickel	1452° C.	0.30
Cobalt	1480° C.	0.21
Iron	1530° C.	0.32
Rhodium	1950° C.	0.00
Tungsten	3400° C.	0.35

It would also be interesting to include the values for platinum and palladium in the table.

We notice, for example, that for the metals cadmium and lead, the melting points of which differ by only 6.4° C., the overvoltage differs by 0.11 volt, whilst for bismuth and tungsten, the melting points of which differ by 3129°, the difference of overvoltage is only 0.15 volt!

Kingsbury Close,
London, N.W.9.

STUDIES IN THE REACTIONS OF THE AMINO GROUP IN 4′ AMINO 1 PHENYL 5 METHYLBENZOTHIAZOLE.

Part XI.—Derivatives of Dehydrothiotoluidine.

By R. F. Hunter, B.Sc., A.R.C.Sc., M.S.Chim., F.C.S.

This paper constitutes the last contribution to the investigation on the reactions of the amino group in 4′ amino 1 phenyl 5 methylbenzothiazole, or dehydrothiotoluidine. As has been intimated in the past papers, the dehydrothiotoluidine necessary for the experiments in connection with this study was worked up from the commercial article by extracting with alcohol, filtering, concentrating and pouring the concentrated extract into water, when the base free from what we regard as the primulines was obtained as a yellow precipitate which dries to a pale white powder, which, however, melts low but appears pure enough for ordinary purposes as it is free from known impurities involved in the production of dehydrothiotoluidine, that is, toluidine, sulphur and primulines. Unfortunately, the matter is not so simple. It will be noted that the combustions were not recorded in the papers published on this investigation, and this was due to the fact that the compounds prepared persistently burnt high sulphur, the error often amounting to 3 per cent. above the calculated value in simple derivatives of the type of

the acetyl benzoyl and benzalamino derivatives. Ultimately a number of estimations of sulphur in dehydrothiotoluidine obtained by water precipitation of alcoholic extractions were made, and here the explanation was found, for the samples gave figures nearly 2 per cent. above the calculated value for sulphur. It was thought that the trouble might be due to occluded sulphur, though this did not appear likely, and consequently some of the derivatives were dissolved in xylene, copper foil added, and the mixture refluxed for some time. The results were, however, quite negative, and the copper quite unaffected. This eliminates the possibility of occluded sulphur. Primuline is insoluble in alcohol, and hence the trouble cannot be due to primuline. The presence of thiotoluidine itself in the dehydrothiotoluidine would scarcely affect the sulphur figures, since the calculated values for dehydrothiotoluidine and thiotoluidine are nearly identical. The figures for the derivatives of dehydrothiotoluidine are worst, and, as has been intimated in the cases of 4′ acetylamino 1 phenyl 5 methylbenzothiazole, prepared by acetylating with acetic anhydride under a reflux for five to ten minutes 4′ benzoylamino 1 phenyl 5 methylbenzothiazole, prepared by the Schotten Baumann method, and 4′ benzalamino 1 phenyl 5 methylbenzothiazole prepared by condensation with the theoretical benzaldehyde in alcoholic solution, when the condensation product separates in 90 per cent. yield, followed by either dissolving in alcohol and precipitating with water, all give figures for sulphur estimations in the neighbourhood of 3 per cent. above the calculated value. Facts such as the above make it clear that the investigation must be abandoned until a method has been devised for preparing the absolutely pure dehydrothiotoluidine in large quantities, and at this point, it can be stated quite fairly that to attempt to work up dehydrothiotoluidine from the dye intermediate by crystallisation from alcohol and, it would appear from the author's experience, with the majority of solvents, including acetone, amyl and methyl alcohols and the others recommended in the literature, is quite hopeless as a laboratory preparation. The method of working up by the thionation of p-toluidine and the modified Casella patent process, that is by 30 per cent. sulphuric acid, described by the author, (*J.C.S.I.*, 1923, XLII., 302) is equally hopeless as a laboratory preparation, for the yield of crude Casella dehydrothiotoluidine never exceeds 30 per cent., and this has to be crystallised twice from alcohol and then boneblacked with boiling acetone and allowed to crystallise, and owing to the great difficulties frequently experienced in crystallisation of the thiazole, the yield is frequently little more than enough to take a melting point determination of the substance. Nevertheless there are certain observations which it is desired to record before the conclusion of this work, and these are connected with derivatives of dehydrothiotoluidine.

Since dehydrothiotoluidine condenses with carbon disulphide in the presence of alcoholic potash with the elimination of hydrogen sulphide to give a body which is presumably di (1 phenyl 5 methylbenzothiazole) thiocarbamide, we should expect the condensation product to form a brom addition product, which probably has the constitution (1) on bromination in alcoholic or glacial acetic acid solution.

$$[CH_3C_6H_3 \lessdot_{NBr}^{S} \gtrdot CBr\ C_6H_4NH]_2:C:S$$

(1)

Actually in alcoholic solution the thio urea forms a brom addition product, a brown solid of moderate stability which is precipitated instantly from the alcoholic solution on the addition of bromine. Dehydrothiotoluidine also benzoylates in the usual way in the Schotten Baumann reaction, the benzoyl compound on treatment with sulphuric acid and ethyl alcohol on warming gives ethyl benzoate. Dehydrothiotoluidine acetylates normally, by refluxing a solution of the base in a mixture of acetic anhydride and acetic acid for some time. The solubility of the acetyl compound in alcohol is poor, but it can be crystallised from ethyl acetate. On adding arsenic chloride to a solution of dehydrothiotoluidine in toluene, a bright orange precipitate is obtained, which can only be filtered with difficulty, dries to a brown solid and contains arsenic and may possibly be (2).

$$[CH_3C_6H_3 \lessdot_{N}^{S} \gtrdot C\ C_6H_4NH]_3:As. \quad (2$$

Dehydrothiotoluidine yields a quinoline by Skraup's reaction, and the latter readily nitrates to give a pale yellow nitro derivative with fuming nitric acid. An alcoholic solution of the base, prepared by the condensation of the dehydrothiotoluidine with chloroform and alcoholic potash, which is assumed to be the isocyanide, forms a brown brom addition product when the solution is brominated. The brom addition product can be purified by washing with ether, and appears to be quite stable in the dry state, and is probably (3).

$$CH_3C_6H_3 \left< {}^{S}_{NBr} \right> CBr\ C_6H_4NC \qquad (3)$$

Dehydrothiotoluidine yields 4′ hydroxy 1 phenyl 5 methyl benzothiazole by the usual reactions, the phenol readily yields a white acetyl derivative with acetic anhydride and sodium acetate, and forms a brom addition product assumed to be (4)

$$CH_3C_6H_3 \left< {}^{S}_{N} \right> CBr\ C_6H_4OH \qquad (4)$$

when an alcoholic solution is brominated.

4′ Benzalamino 1 phenyl 5 methylbenzothiazole obtained by the condensation of dehydrothiotoluidine with benzaldehyde in alcoholic solution should on thionation yield the bis benzothiazole (5) in the usual way, the mechanism being presumably ortho substitution of sulphur and the elimination of the hydrogen atom of the benzaldehyde residue and of the ortho hydrogen with an atom of sulphur as hydrogen sulphide.

$$CH_3C_6H_3 \left< {}^{S}_{N} \right> C\ C_6H_3 \left< {}^{S}_{N} \right> C\ C_6H_5.$$

Actually, thionation of benzaldehydrothiotoluidine produces a base which is extracted by 60 per cent. sulphuric acid and which gives a yellow alcoholic fluorescent solution.

Lastly, with regard to the nitration of dehydrothiotoluidine, it will be recalled (*The Chemical News*, 1924, CXXVIII., 88) that a base was isolated which dissolved in alkali and ammonia, and was reprecipitated by the addition of alkalis. The nitration was repeated at a later date, as described in the experimental part of this paper, and it was found that the nitro compound so produced was insoluble in ammonia and alkalis, but was crystallisable in red-brown crystals from hot benzene, and was quite different from the base described in the earlier paper. *These facts were explained* at a later date, however, during the preparation of a large quantity of nitrodehydrothiotoluidine, when it was discovered that when the nitration was carried out under very vigorous conditions with fuming nitric acid, there were produced two substances, one of which dissolved in alkalis and was reprecipitated by alkalis, the other of which was the ordinary nitro compound. The alkali soluble base is quite different in properties, and has a most unpleasant odour reminiscent of that sometimes experienced in the oxidation of indigo with nitric acid to isatin. The odour is heavy and very unpleasant and suggestive of some nitrogen heterocyclic base.

Now with regard to the hydrolysis of dehydrothiotoluidine, it is clear that on alkali fusion dehydrothiotoluidine should break up according to

$$CH_3C_6H_3 \left< {}^{S}_{N} \right> C\ C_6H_4NH_2$$
$$\rightarrow \quad CH_3C_6H_3\ (SH)\ NH_2$$

(5)

into the thioaminocresol and *para-amino-*benzoic acid. This is what actually happens, the thiazole ring being first broken between the double-bonded nitrogen and carbon atoms, and then being ruptured at the linkage between the carbon atom which carries the nitrogen and sulphur atoms in the thiazole ring, and the sulphur atom, with the production of the aminothiocresol. The aminothiocresol formed by the breaking up of dehydrothiotoluidine possesses actually an odour very similar to the base obtained as a by-product when nitration is allowed to proceed too vigorously, and it would appear likely that the base referred to above is a substance produced by the oxidative fission of the fused thiazole ring in dehydrothiotoluidine, since it is well known that the nitro derivatives of dehydrothiotoluidine itself are odourless. With regard to the breaking up of the benzothiazole by alkali fusion, it is recommended to carry out this reaction in a fume cupboard, to wear rubber gloves when handling the products, and not to expose

the face unduly to the action of the fumes evolved in the reaction, which have a very deteriorating effect on the skin, bringing out a type of eczema which may last for as long as a fortnight, and which leaves the skin in a very enfeebled condition when the blisters break. Incidentally it is desired to emphasise the fact that hot solutions of dehydrothiotoluidine should not be handled carelessly, as such solutions, in contact with the hand, produce a very unpleasant type of eczema which is most severe between the fingers, and which may become severe enough to necessitate the suspension of the investigation for short periods.

Experimental.

Dehydrothiotoluidine.

150 gms. of the dye intermediate are extracted with a litre of spirit under a reflux for ten minutes, and the solution poured into an equal volume of water, the precipitate allowed to stand and filtered at the pump. Melts low. Analysis:

S per cent. Calculated = 13.3 per cent.
S per cent. found = 15.1 per cent., 14.9 per cent., 15.1 per cent., 15.1 per cent., 15.2 per cent., 15.2 per cent.

Dehydrothiotoluidine was dissolved in xylene in a flask fitted with a reflux condenser, clean copper foil added, and the mixture refluxed for half-an-hour with negative results. The solution was then removed and allowed to stand on the steam for a day with negative results. Clearly, then, occluded sulphur is absent from the compound.

4′ Acetylamino 1 phenyl 5 methylbenzothiazole.

5 gms. of dehydrothiotoluidine were dissolved in 30 ccs. of acetic anhydride in a flask fitted with a condenser, and the mixture refluxed on a sand bath for five minutes. The solution poured while hot into 300 ccs. of cold water, the acetyl derivative is precipitated as a dirty white substance. The mixture is allowed to stand for two hours, stirred, filtered, washed with warm water and dilute alcohol. The solubility in alcohol is rather poor, and alcoholic solutions do not crystallise readily. The acetyl derivative is taken up in alcohol and the solution poured into water, the white precipitate being filtered and dried. Yield: practically theoretical.

A portion was refluxed for some time with ethyl acetate, and the solution cooled and allowed to crystallise. The crystals were, however, of a poor quality.

S estimation for the precipitated substance about 3 per cent. high on the average.

4′ Benzoyl amino 1 phenyl 5 methylbenzothiazole.

4 gms. of the thiazole are mixed with 25 ccs. of 2N caustic soda in a conical flask fitted with a tight cork, the mixture warmed, and 4 ccs. of benzoyl chloride added slowly with steady shaking and warming over a period of half-an-hour, the excess benzoyl chloride being finally destroyed with warm alkali. The mixture is poured into 200 ccs. of cold water, the ochre precipitate collected, washed, dried, dissolved in alcohol, and the solution poured into water and the precipitate collected. A portion recrystallised from alcohol in pale yellow crystals, without the usual troubles of "tarring." Acids cause hydrolysis of the compound, sulphuric acid, and alcohol gives the odour of ethyl benzoate on warming. S estimation, about 3 per cent. high.

4′ Benzalamino 1 phenyl 5 methylbenzothiazole.

5 gms. of dehydrothiotoluidine were dissolved in about 200 ccs. of alcohol, the solution refluxed on a boiling water bath, while the theoretical benzaldehyde was run in; the mixture refluxed for another ten minutes, and the yellow solution cooled. Yellow crystals of the condensation product separate. Yield, over 90 per cent.

The benzal compound is taken up in alcohol and the solution poured into water, the precipitate filtered and dried, but burns sulphur, which is more than 3 per cent. above the calculated value.

The benzal compound is readily hydrolysed with boiling 40 per cent. sulphuric acid, and benzaldehyde can be isolated from the steam distillation products. The benzal compound, when dissolved in alcohol and brominated, yields a brown precipitate of the brom addition product of the thiazole.

4′ Hydroxy 1 phenyl 5 methylbenzothiazole.

5 gms. of dehydrothiotoluidine are treated with 25 ccs. of concentrated hydrochloric acid in a flask, 50 ccs. of ice water are added, and the theoretical sodium ni-

trite in ice water run in, the mixture shaken, and the flask heated for two hours on a boiling water bath. The contents are then rinsed into a beaker with caustic soda solution, excess of alkali added, the solution of the phenol diluted to 400 ccs. and filtered from brown colloidal matter overnight. The alkaline solution is then treated with concentrated hydrochloric acid, added drop by drop, until no more precipitation takes place. The precipitate is filtered and washed and dried. The crude phenol so obtained is then refluxed with alcohol and animal charcoal for half-an-hour, the alcoholic solution poured into cold water, and the white precipitate filtered and dried. Yield, 50 per cent.

The alkaline solution of the phenol will not couple with diazotised sulphanilic acid, owing to the fact that the para position is blocked by the tolylthiazole residue.

Condensation of dehydrothiotoluidine with carbon disulphide.

5 gms. of the base are dissolved in 120 ccs. of alcohol and 30 ccs. of carbon disulphide, to which 1 gm. of potassium hydroxide has been added, in a 500 cc. round-bottomed flask fitted with a long reflux condenser, and the flask heated for four hours on a boiling water bath. Hydrogen sulphide is evolved during the condensation, and the liquid darkens as the reaction proceeds. The liquid is then transferred into a distilling flask, concentrated, and allowed to cool and crystallise. The orange crystals are filtered off, and are nearly insoluble in alcohol. The condensation product is then refluxed with 100 ccs. of alcohol for ten minutes, to remove any traces of unchanged aminothiazole, the mixture is allowed to cool and the crystals filtered off and dried. An alcoholic solution of the substance displays a fine fluorescence, particularly to ultra-violet light.

Bromination.

An alcoholic solution of the thio urea is prepared and brominated by adding bromine drop by drop from a burette, when a brown brom addition product separates, which is filtered, washed and dried, and appears stable at ordinary temperatures.

Condensation of dehydrothiotoluidine with chloroform and alcoholic potash.

5 gms. of dehydrothiotoluidine are dissolved in 200 ccs. of alcohol to give a clear yellow solution, a small quantity of potassium hydroxide is added, the solution transferred to a flask fitted with a condenser and heated to boiling on a water bath. About 10 ccs. of chloroform are slowly run into the boiling solution. The solution is refluxed for five hours and then allowed to cool, when greyish coloured crystals separate. These are filtered off and recrystallised from alcohol in small pale yellow crystals. The solution of the compound in alcohol betrays a beautiful fluorescence.

A solution of the isocyanide in alcohol is brominated by adding bromine drop by drop from a burette with stirring, the addition product separates as a brown coloured precipitate, which is filtered, washed and dried, and appears stable at ordinary temperatures.

Action of arsenic chloride on a toluene solution of dehydrothiotoluidine.

2 gms. of dehydrothiotoluidine are dissolved in toluene by warming under a reflux condenser, the solution cooled to room temperature if any base settles out. More toluene must be added to complete the solution. 2 ccs. of pure arsenic chloride are then added slowly drop by drop. The first drop of chloride produces an orange precipitate. The suspension is allowed to stand ten minutes and then filtered overnight, and finally dried to a brown solid between filter papers.

Nitration of the quinoline of dehydrothiotoluidine.

The quinoline prepared as described (*loc. cit.*) is dissolved in fuming nitric acid, and the nitric acid solution poured into cold water when a yellow precipitate is obtained which is filtered and dried.

The thionation of 4′ benzalamino 1 phenyl 5 methylbenzothiazole.

10 gms. of dehydrothiotoluidine are mixed with 100 ccs. of alcohol and the suspension boiled under a reflux condenser, when the theoretical benzaldehyde is run down the condenser with a little alcohol. The mixture is boiled for fifteen minutes, poured into a beaker and allowed. The crystals of the benzal condensation product are filtered and dried.

8 gms. of the benzal compound so prepared are mixed with 2 gms. of sulphur in a 250 cc. round-bottomed flask fitted with an air condenser. The flask is heated in

an oil bath for two hours at 255° C., when torrents of hydrogen sulphide are evolved in the first stages of the reaction. The flask is removed and allowed to cool. To the cool melt in the flask is then added 30 ccs. of hydrochloric acid (concentrated) and the air condenser changed for a water condenser and the mixture refluxed on a sand bath for half-an-hour. The extract is filtered through glass wool into cold water, but the precipitation of dehydrothiotoluidine is negligible. The melt is removed, pulverised, and extracted with three 30 cc. portions of 60 per cent. sulphuric acid, and the extracts filtered through asbestos into a flask containing about 200 ccs. of water. Strong ammonia is added until the filtrate is alkaline, and the bright chrome precipitate filtered, washed with a little dilute ammonia, water, and then dried.

The substances dissolve in hydrochloric acid to give a brown solution, and in hot alcohol to give a splendidly fluorescing yellow solution.

The nitration of dehydrothiotoluidine.

5 gms. of dehydrothiotoluidine are slowly added to 35 ccs. of fuming nitric acid in a 140 cc. beaker with good stirring. Heat and nitrous fumes are evolved during the addition. The brown solution which results is allowed to stand for two hours and then poured into 400 ccs. cold water. A deep orange precipitate is allowed to stand, and is filtered, washed and dried. The nitrate of the nitro compound so obtained is placed in a 350 cc. beaker and treated with 200 ccs. of dilute ammonia. The mixture turns a red brown colour. The suspension is warmed and stirred, allowed to stand for some time, and then filtered. Acidification of the alkaline filtrate does not produce precipitation. The free nitro compound is well washed, dried, and a portion recrystallised in brown red crystals from benzene.

Repeating this on a larger scale with dehydrothiotoluidine, which still contained a faint trace of dilute alcohol, the reaction was much more violent. On pouring the mixture into water, a most unpleasant odour was observed. On treating the nitrate of the nitro compound with ammonia, a small amount of the substance dissolved. Acidification produced a brown precipitate which, even in the dry condition has an unpleasant odour reminiscent of that of aminothiocresol obtained by the alkali fusion of dehydrothiotoluidine. The nitro compound dissolves in glacial acetic acid, from which it is precipitated by the addition of ammonia or caustic soda solution. A glacial acetic acid solution of the nitro compound, on bromination in the usual way by adding bromine drop by drop from a burette charged with the liquid halogen, deposits a brom addition product of the usual type. There is, however, a strong tendency to tar up, and the addition of bromine must be carefully regulated.

The physiological action of dehydrothiotoluidine.

Hot solutions of dehydrothiotoluidine in contact with the skin develop an unpleasant form of eczema. The effect is worst between the fingers of the experimenter, and the irritation is particularly intense during the first few days. The blisters finally break, liberating an infectious liquid, which spreads the trouble. Bathing in hot water takes down the irritation to a certain extent. Observations on this effect have been made by other investigators in the field of benzothiazoles. Thus Hofmann (*Berichte*, 1887, XX., 2251), at the end of one of his papers, states that the vapours of aminophenylmercaptan have a most detrimental effect on the skin, producing intense irritation and swelling, the affectation spreading to all parts of the body which come into contact with the affected part. Baumann (*Berichte*, 1887, XX., 2251) states that in his work on mercapturic acid the effect was so severe that he had to give up his researches over a number of periods. Bathing the infected parts with 2 per cent. phenol also has a beneficial effect. The vapours of dehydrothiotoluidine evolved during its distillation have a similar irritating effect on the throat and chest. The thionation of acetanilide, it might be mentioned at this point, also produces irritating vapours, which have an unpleasant effect on the skin of the hands, and the throat and chest. It is advisable to carry out all caustic alkali fusions of benzothiazoles in a good draught cupboard, or, better still, in the open.

In conclusion, it might be stated that it is hoped at a later date to obtain sufficient pure dehydrothiotoluidine to repeat the preparations which have been described in the papers on the reactions of the amino group in 4′ amino 1 phenyl 5 methylbenzo-

thiazole, and to obtain the compounds, many of which are new in a sufficient state of purity to confirm the suggested structures.

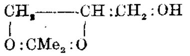
The Chemical Laboratory,
Highbury New Park, N.5.
June, 1924.

PROCEEDINGS AND NOTICES OF SOCIETIES.

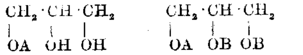
SOCIETY OF CHEMICAL INDUSTRY.

(*Concluded from Page 74.*)

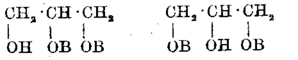
The synthesis of glycerides of definitely known structure is complicated by the possibility of internal rearrangement and the wandering of acyl groups in the molecule. Fischer has used acetoneglycerol:—



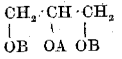
as the starting-point for the preparation of α-monoglycerides such as α-monolaurin, α-monopalmitin, α-monostearin. These are readily converted into such triglycerides as α-lauro-α′β-distearin on treatment with the corresponding acid chloride and quinoline or pyridine:—



Under similar conditions the α-iodohydrin gives a diacyl derivative, presumably αβ, which, however, owing to the wandering of an acyl group, changes to the symmetrical αα′ derivative:—

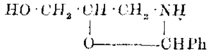


On introducing the third acyl group A the final product:—



is isomeric with that above, having a higher melting point and lower solubility in accord with its symmetrical structure.

A method for the preparation of mixed glycerides, in order to be of many-sided applicability, must be of such a nature that the three OH groups of the glycerol can be so differentiated that it is possible to treat them differently at the individual stages of the process; the starting material must, therefore, be such that two of three substitutable groups in the glycerol are at first masked and are uncovered only in the further course of the synthesis and then only successively. A substance fulfilling these rehuirements is the compound 2-phenyl-5-hydroxymethyloxazolidine:—



suggested by Bergmann, which has but one alcohol group available for esterification. A second, however, can be produced by the action of acids, whereby it is hydrolysed to benzaldehyde and aminopropyleneglycol, $HO \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot NH_2$, and finally the third is produced by treating the last compound with nitrous acid.

The actual physical properties of a fat are due to the nature of the glycerides of which it is composed. Two fats may contain the same acid radicals in much the same proportions and yet appear very different in texture, melting point, etc.—factors which are of the greatest importance in their technical application. Thus analyses of cacao butter and of South American mutton tallow made in our laboratories show that the percentage of fatty acids obtained from them is very nearly the same and yet the two fats are entirely different:

	Cacao butter.	Mutton tallow.
Myristic acid	0	1.5
Palmitic acid	23.2	21.0
Stearic acid	33.6	30.0
Oleic acid	41.8	43.0
Linoleic acid	1.4	5.0

Crystallisation from solvents has been the usual means of effecting the separation, but a far more satisfactory method is required. We would go so far as to say that this is the most pressing practical problem awaiting solution in this field of inquiry.

The glycerides in butter fat are mainly mixed glycerides. Oleopalmitobutyrin has been isolated, and it is probable that the

whole of the butyric acid found in the fatty acids exists in this form. The mixed glycerides in lard have been carefully studied by Amberger and Wieschahn, who have compared those isolated with those synthesised and those obtained by their hydrogenation. They have identified the presence of:—

β-Palmito-αγ-distearin.
β-Stearo-αγ-dipalmitin.
α-Oleo-βγ-distearin.
α-Palmito-βγ-diolein.
β-Oleo-α-palmio-γ-stearin.

Beef fat contains tristearin, distearopalmitin, and dipalmitostearin (Dekker).

In palm kernel oil, Bömer has identified the presence of the following glycerides:—

Caprylmyristo-olein,	m.p. 14°
Dilauromyristin,	m.p. 33°
Laurodimyristin,	m.p. 40°
Dimyristopalmitin,	m.p. 45°
Myristodipalmitin,	m.p. 51°

Oleodistearin and oleodipalmitin are said to be constituents of cacao butter; in addition, it must contain either triolein or glycerides containing two molecules of oleic acid.

A lengthy account of the distribution of fatty acids in nature then followed

THE FORMATION OF THE FATTY ACIDS.

The evidence we have discussed in the foregoing, apart altogether from the occurrence of the fats as mixed glycerides, indicates the great variety there is in the proportions of the fatty acids, and often in their nature between different species, both of plants and animals, and yet the fat of any one species is remarkably constant in composition. Any mechanism of the syntheses of fats must take such facts into consideration, and must in addition solve these problems:—

(1) The formation in certain cases, in both the plant and the animal, of acids consisting of all the lower even members of the series.
(2) The formation of C_{18} acids, sometimes together with varying proportions of C_{16} and C_{20} acids.
(3) The formation of oleic acid and the reason for the position of the ethenoid bond in the middle of the chain.
(4) The formation of a high proportion of very unsaturated acids which appears to involve further the occurrence of acids with more than 18 carbon atoms.

We shall seek to give tentative answers to these questions solely with the desire of indicating a number of possibilities so as to attract attention and encourage further work on this subject.

Broadly speaking, the evidence we have quoted, which is contained in Table III., though it is at present incomplete, shows the distribution of these acids to be much as follows:—

A. C_{21} and C_{14} acids present in considerable quantity.—The C_{12} and C_{14} acids of the nut oils are almost exclusively saturated, any unsaturated component being as a rule olein C_{18}.

B. 25-40 per cent. C_{16} and the rest C_{18}. Unsaturation monoethenoid, diethenoid also often present, but found both in plants and animals.

C. Almost all C_{18}. — Unsaturation mono- to tri-ethenoid. Usually very little stearin present. Occur practically only in vegetable oils—olive, soya, maize, linseed, Chinese wood oil.

D. Some C_{16}. — Unsaturation monoethenoid.
Much C_{18}.—Unsaturation mono-, di- and (query) tri-ethenoid.
Considerable C_{20} and C_{22}.—Unsaturation mainly tri- to hexa-, (query) mono- and di-ethenoid.
Occurrence mainly in marine animal oils.

Our survey leads us to advance as one tentative hypothesis for discussion that fats are synthesised in plants and in animals from carbohydrates, the unit attacked being the primary or basic C_{18} complex of starch, which workers in the field of carbohydrate chemistry now consider to be the nucleus of most polysaccharides, rather than the simple C_6 unit of glucose. The C_{18} unit, consisting of three C_6 units united through oxygen atoms, undergoes internal rearrangement, oxidation and reduction, at which moments the rupture of the oxygen bridge and the joining of carbon to carbon might take place.

The product would probably be stearic acid, oleic acid appearing at a later stage. The formation from this of homologous

acids higher and lower, both saturated and unsaturated, with an even number of carbon atoms might be explained perhaps by the processes of β-oxidation and aldol condensation, which we shall shortly disucss. Such reactions appear very complicated in our present state of knowledge, but they are akin to those which take place during fermentation, of which our information is rapidly increasing, though we have far to go before the change from CH(OH)- to CH_2- is understood. It should further be remembered in connection with the formation of several acids at the same time that ferment actions, even *in vitro*, are never simple actions, but are always accompanied by other secondary changes.

A second type of fat synthesis which we must consider is perhaps that which produces milk fats and such vegetable oils as the nut oils, *e.g.*, coconut and palm kernel oil. Here the mechanism is such as to lead to the formation of all the lower members of the series with an even number of carbon atoms, the action taking place in a solution of simple carbohydrate (sugar, not starch). The most simple explanation of such a series appears to be the building up of the acids from one another by repeated aldol condensation.

In the formation of butter fat, for example, something akin to a butyric acid fermentation of sugar may be taking place. On the other hand, the possibility of a progressive far-reaching degradation from a C_{18} acid to the lower acids must not be excluded as an alternative.

It was suggested originally by Nencki that in the butyric fermentation of lactic acid the latter splits up into a molecule of formic acid and a molecule of acetaldehyde, thus:—

$$CH_3\cdot CH(OH)\cdot CO_2H = CH_3\cdot CHO + H\cdot CO_2H.$$

Two molecules of aldehyde then unite to give butyric acid:—

$$CH_3\cdot CH(OH)\cdot CH_2\cdot CHO \rightarrow CH_3\cdot CH_2\cdot CH_2\cdot CO_2H.$$

Higher fatty acids should be formed by a further union of aldehyde molecules and ensuing reduction, so that the butyric fermentation would represent the first stage of a reaction which gives rise to the higher fatty acids with an even number of carbon atoms. The facts that *n*-hexoic (caproic) and *n*-octoic (caprylic) acids were shown by Raper to be regular products of the butyric fermentation support this view, though there is no laboratory evidence of the process giving rise to the higher acids in quantity; it may be urged that it should be possible to obtain this, seeing that C_{12} acids are the chief products in the coconut and other palms. The action involved in the reduction of the β-alcoholic hydroxyl, accompanying the oxidation of the aldehyde group, is apparently a general one in carbohydrate metabolism.

The fact that under certain abnormal conditions fatty acids with an uneven number of carbon atoms are degraded to propionic acid, and this is metamorphosed through lactic acid to glucose, leads us to suggest yet a third hypothesis for the synthesis of fats, in the same tentative manner, of course, as our other hypotheses. It is that glucose is resolved into a C_3 unit and these C_3 units are condensed to fatty compounds or substances approximating to them with 6 and with 9 carbon atoms—such units immediately combine with themselves to form units with 12 or 18 carbon atoms. In such a synthesis oleic acid might be the penultimate stage; we have difficulty at the moment in accounting for the ethenoid bond in the centre of the chain in any other fashion. The supposition that it arises by migration of an ethenoid linkage from the 2:3 position is one which we find difficulty in accepting. The condensation to a C_{12} unit would account for such fats as occur in the coconut and the palm kernel and in milk fat, the C_{18} unit being the product in the case of other vegetable and animal oils which it will be observed contain no C_{12} acids and only small quantities of C_{14} acids.

The chemist is particularly interested in the fact that only fatty acids with an even number of carbon atoms are found, and further, that oleic and stearic acids are constituents of all fats, whatever other acids may be present. It would appear that whatever may be the mechanism of synthesis, there is a tendency to form compounds with 18 carbons, produced, it may be, from three molecules of glucose, either as such or in the form of the nucleus of starch. The other fatty acids may be formed by secondary reactions from the C_{18} molecule; there would be reason to expect much the same mixture of acids in all fats,

at least qualitatively, if the same mechanism were concerned in every case. There is a good deal known about such secondary changes, particularly in relation to the theory of β-oxidation first enunciated by Knoop and subsequently elaborated by Dakin.

If it be admitted that C_{18} acids are derived from starch or from glucose by one of the processes suggested, the method of formation of palmitic acid, C_{16}, and the higher acids, C_{20}, C_{22}, C_{24}, requires some consideration.

The summary on page 3 indicates that *increasing* unsaturation is roughly a function of the length of the chain, and that C_{18} acids are not really much more in evidence when other acids are present with them than are the lower and higher members.

Palmitic acid may well be formed as the *result of a β-oxidation process*, and when palmitoleic and myristic acids accompany it we are inclined to this view. In other cases, some mechanism to account for its direct synthesis seems desirable; this we are not yet in a position to suggest.

The formation of higher acids, C_{20} to C_{24}, *is still more difficult to explain*—since Hartley found them in the pig's liver derived in all probability from C_{18} acid in the tissues—they may perhaps arise by the condensation of small fractions produced during the oxidation of stearic acid *in vivo*. The location of the ethenoid linkings has to be determined before such questions can be answered.

In vivo, in the animal, the hydrogen attached to the β or the third carbon atom of a fatty acid is selected for oxidation so that a long chain compound loses two carbon atoms every time. For example, phenylvaleric acid becomes phenylpropionic acid, and this in turn benzoic acid. Butyric acid is converted first into β-hydroxybutyric acid and then into acetoacetic acid:—

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CO_2H \rightarrow CH_3 \cdot CH(OH) \cdot CH_2 \cdot CO_2H \rightarrow CH_3 \cdot CO \cdot CH_2 \cdot CO_2H.$$

An exactly similar change is brought about by hydrogen peroxide, as shown by Dakin, when β-keto-acids and the corresponding ketones are formed. This is, however, not the only action of hydrogen peroxide, as there is undoubtedly some oxidation in both the α- and the γ-position.

Working with stearic acid, Clutterbuck and Raper show that the relative amounts of the acid undergoing β- and γ-oxidation are of the order 7 to 1 respectively. It is suggested that γ-oxidation may also take place in the body, but Dakin considers that all the physiological evidence is against this.

Embden has shown that in the liver acetoacetic acid is only formed from the higher fatty acids with an *even* number of carbon atoms; this is not only a striking confirmation of Knoop's theory, but also indicates that the degradation of the higher acids is progressive, two carbons being split off each time, and that there is no break in the middle of the chain in oleic acid, for example, which might lead to the formation of C_9 units.

A clue to the mechanism of the oxidation of the fatty acids which contain an *uneven* number of carbon atoms is afforded by Ringer's proof that in diabetic organisms they are converted into glucose about in proportion to the amount of propionic acid they might furnish through β-oxidation. According to the evidence, propionic acid is presumably converted into lactic acid or pyruvic acid, and it is well known that the former is quantitatively and the latter partially converted into glucose in the diabetic organism.

The mechanism of β-oxidation has been fully studied by Dakin, who has proved that $\alpha\beta$ unsaturated acids are formed in the animal body either indirectly through the intermediate formation of hydroxy-acids or directly.

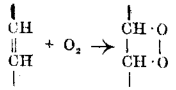
In the liver, as Hartley's work has shown, unsaturated acids are formed both from stearic and oleic acids by the introduction of an ethenoid bond between carbons 12 and 13. If oleic acid is formed in nature from stearic, it follows that the ethenoid bond is introduced between carbons 9 and 10, and in linseed, as Eyre has proved, unsaturated acids are formed during ripening. The question arises as to whether these ethenoid bonds are introduced in their final positions at specific points of weakness in the chain of carbon atoms or whether there has been a migration of the bond from some other point where it was first formed to its present position.

It would lead us too far to discuss the migration of ethenoid bonds—a phenomenon well known to the organic chemist—but the conversion of oleic acid into palmitic

and acetic acids, together with smaller quantities of lower homologues of palmitic acid on fusion with potash, a reaction involving both oxidation and shifting of the ethenoid link, may be recalled in this connection.

There is a good deal of evidence known to the organic chemist that acids of a homologous series show an alternation in properties between the odd and even members. This applies to the dibasic acids of the oxalic series as well as to the monobasic fatty acids, as Challenor and Thorpe have shown. In the former instance, in addition to differences in physical properties, another property is the ease with which the even members of the series are produced by the direct oxidation of suitable substances, whereas the yield of the odd members is very small, except under carefully regulated conditions, the substance being oxidised to the next lower even number. Thus ricinoleic acid, on oxidation with nitric acid, yields azelaic acid, $C_9H_{16}O_4$, and suberic acid, $C_8H_{14}O_4$, in about equal proportions, although theoretically only azelaic acid should be obtained. The authors quoted consider that in the light of recent theories of polarity azelaic acid is much more reactive than suberic acid, and is thus more readily oxidised, giving an even member of the series. They give examples of the tendency of an even carbon chain to lose 0, 2, 4, etc., atoms of carbon on oxidation, and of an odd carbon atom chain to lose 1, 3, 5, etc., atoms, the product in all cases belonging to the even series.

An understanding of the mechanism of oxidative and reducing changes in tissue as yet eludes us, though some light on the subject has been thrown by the experiments of Hopkins on the behaviour of glutathione. Hopkins and Dixon were able to show that a system composed of thioglycollic acid and dried muscle powder was very active in taking up oxygen, but that the muscle lost this power after extraction with alcohol and ether. Meyerhof has shown that the active constituent of the muscle was linolenic acid, which is able to take up two molecules of oxygen to each molecule of acid. As only one pair of double bonds disappears, these must therefore have been oxidised to a peroxide linking



as is known to occur in the spontaneous oxidation of linolenic acid.

It must be remembered in this connection that Coffey and also Morrell have shown that in presence of a drier the oxidation of linoleic acid and also of linolenic acid is restricted to the absorption of one molecule of oxygen instead of two.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

[TORONTO MEETING.]

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCE.

PROF. A. FOWLER, F.R.S.—*The Spectra of Ionised Elements.*

The paper gives a summary of recent work on the spectra of ionised and multiply-ionised atoms. In the case of silicon, four successive spectra have been sufficiently observed to permit the complete or partial classification of the lines in series. In passing from Si IV to Si I, the effects of adding external electrons one by one are exhibited under somewhat simpler conditions than in the regular sequence of the neutral atoms of Na, Mg, Al, and Si, since the charge and the mass of the nucleus remain constant. Similar changes in the spectra of other elements have been observed, and series have been worked out for C II. The ionisation potentials deduced from the series of silicon and carbon have an important application in connection with the determination of the temperatures and densities of stellar atmospheres.

DR. F. L. MOHLER and DR. P. D. FOOTE. —*Critical Potentials and their Interpretation.*

Available data on the normal energy levels of atoms, particularly in the range inaccessible to spectroscopic methods, are summarised. Results obtained in this laboratory on radiation potentials of gases and stages in the excitation of spectra are compared with critical radiation potentials of solids and other data on soft X-ray limits.

Moseley diagrams of these limits give curves of the type predicted by Bohr.

Some questions as to the interpretation of critical potentials can be settled on the basis of this correlation of results.

PROF. J. C. McLENNAN, F.R.S.—*Recent Studies in Band Spectra and their Bearing on the Structure of Molecules.*

MR. R. H. FOWLER.—*Mechanisms of Excitation, Ionisation, and Dissociation in Statistical Theory.*

DR. R. J. PIERSOL.—*Pulling Electrons from Metals by Intense Electric Fields.*

DR. ANNE C. DAVIES.—*The Metastability of the Fundamental Coplanar Condition of the Helium Atom.*

Further experimental evidence bearing on the conclusions of Horton and Davies that an emission of radiation results from the displacement of an electron within a helium atom from the normal orbit (the fundamental orbit of the crossed system) to the first outer orbit (the fundamental orbit of the coplanar system), and that this radiation can be absorbed by normal helium atoms, these conclusions being at variance with the conception of the fundamental coplanar condition of the helium atom as a metastable state.

MR. L. F. RICHARDSON.—*Coronæ and Diameters of Particles.*

Airy, in 1834, gave a theory of diffraction which has been long since applied both to the resolving power of telescopes and to coloured rings sometimes seen round the moon. The present writer has compared the theory with laboratory measurements.

PROF. FRANK ALLEN.—*Visual Sensory Reflexes.*

MR. F. J. W. WHIPPLE.—*An Experiment Illustrating the Theory of the Green Flash.*

When the sun sets under favourable conditions, the last glimpse appears a brilliant green.

The theory that the phenomenon is due to the simultaneous action of dispersion and absorption is now generally accepted. The experiment is designed to illustrate this theory.

SIR RICHARD PAGET, BART.—*The Nature of Speech.*

PROF. P. E. SABINE.—*Research in Architectural Acoustics.*

SIR NAPIER SHAW, F.R.S.—*If the Earth went Dry.*

The phenomena of the general circulation of the atmosphere depend fundamentally upon warming at the surface by the sun's rays, and on cooling these by outward radiation; but the dominant factor of weather is the modification due to water-vapour in the air. In this paper, in order to clear ideas, the reader is invited to regard these two aspects of thermal influence as distinct, and to consider the effect of "dry heat" alone. We thus form an idea of what the general circulation would be if there were no water-vapour at all in the air.

The subject is hypothetical, inasmuch as the actual circulation is generally affected by the condensation or evaporation of water, but its discussion is not necessarily sterile. It is an exercise in some important points of thermal economy; in deserts the conditions postulated are approximately realised, and yet winds, dust-storms, and "dust devils" are not infrequent there; and in the large part of the atmosphere where the temperature is below 270 *t* the relative amount of water-vapour, though not by any means without function, is too small to play the dominant role.

It is assumed that "dry" air (except for dust) would be perfectly transparent. Radiation received by a perfect absorber normal to the sun's rays would be 135 kilowatts per square dekametre (subject to small variations of the solar constant), and the loss of heat from a surface radiating perfectly (subject to local variation on account of dust) would be $0.572 \times (t/100)^4$ kw., and range from 9 kilowatts per (10 metre)^2 for 200 *t* to 46 for 300 *t*. A table is given of the temperatures (between 200 *t* and 402 *t*) at which the loss from a radiating surface would balance the income for given solar altitudes.

SIR FREDERIC STUPART.—*The Variableness of Canadian Winters.*

GENERAL PHYSICS SUB-SECTION.

PROF. A. H. COMPTON.—*The Quantum Theory of the Scattering of X-Rays.*

PROF. J. A. GRAY.—*Scattering of X- and*

Gamma-rays and the Production of X-rays by Photo-electrons.

PROF. W. DUANE.—*On Secondary and Tertiary Radiation.*

This paper gives the results of recent experiments on secondary and tertiary radiation carried on in our laboratory by Doctors Allison, Clark, and Stifler. The experiments with an X-ray tube in one large room radiating through a hole in the wall into a second room that contains the X-ray spectrometer, indicate the presence of scattered radiation, fluorescent radiation, and tertiary radiation only, in the beam of X-rays coming from a secondary radiator. The tertiary radiation has the short wave-length limit that would be expected if it were due to the bombardment of photo-electrons. No other radiation comparable in intensity with these three types appears in the spectra. In case the X-ray tube lies in a small box, the influence of the walls of the box on the spectra is discussed.

Experiments also are described illustrating the reflection by a crystal of X-rays characteristic of the chemical elements in the crystal itself, and the precautions necessary to procure photographic evidence of this characteristic reflection are mentioned.

By placing sheets of copper in the path of the X-rays incident on the crystal sufficient in thickness to cut off practically all the radiation having wave-lengths of the characteristic line spectra of the crystal, it has been shown that this phenomenon cannot be regarded as an increase in the reflecting power of the crystal for certain rays already existing in the primary beam, but must be due to the fluorescent radiation generated in the crystal itself by X-rays of much shorter wave-lengths.

(*To be continued.*)

NOTICES OF BOOKS.

Numerical Examples in Chemistry, by WILLIAM R. FIELDING, M.A., M.Sc. Pp. 108. 1924. 1s. 3d.

Science masters will not need to be reminded of the general dislike of pupils for answering numerical problems and calculations in chemistry.

Mr. Fielding's new little book has many merits to recommend it for use in schools and colleges. The author has commenced with a short introductory chapter giving certain necessary mathematical and physical data and exercises thereon.

Formulæ and equations are then considered, and are followed by exercises in the writing of equations and finding molecular weights with the aid of the atomic weight table.

The subsequent chapters contain examples set upon the following subjects, which are briefly introduced to the student: solution and crystallisation, percentage composition of compounds, calculation of formulæ, densities of gases, use of equations, applications of Boyle's and Charles' laws, equivalents and volumetric chemistry.

Two sets of miscellaneous examples have been taken from the question papers of various examining bodies. Altogether the eleven chapters contain over 500 problems suitable for the requirements of candidates for School and Higher School Certificate, matriculation, and other examinations.

The volume is therefore specially suited for use in secondary schools, and its value is enhanced by the inclusion of the answers, a feature that will commend it to the teaching world. J.G.F.D.

Airs (for the Hautbois and other Instruments), by E. N. DA C. ANDRADE. Pp. VIII. + 68. London: Cecil Palmer, 49, Chandos Street, W.C.2. 1924. 3s. 6d. net.

Most of us have our hobbies, by the cultivation of which we are able to maintain our mental equilibrium. Dr. Andrade evidently devotes his leisure to the composition of verse, a sample of which he gives us in this little volume, and he promises more later—at least he says that if challenged he will write a book of the "latest pattern" and it shall be called "Stinking Fish for Gulls."

The style of the foreword of "Airs" is that of the seventeenth century, and the whole book has a very diverting effect upon the reader.

A Course of Instruction in Instrumental Methods of Chemical Analysis, by WILLIAM N. LACEY. Pp. VII. + 95. London and New York: MacMillan & Company, Ltd. 1924. 7s. net.

The object of this work is to familiarise students with the more important instru-

ments used in industrial organic analysis. These include the microscope, polariscope, refractometer and various pieces of apparatus used in gas analysis, etc.

The book should be of service to lecturers in technical colleges and institutes.

Matter and Change—An Introduction to Physical and Chemical Science, by WILLIAM CECIL DAMPIER WHETHAM, M.A., F.R.S. Pp. VI. + 280. Cambridge: The University Press. 1924. 7s. 6d. net.

The power of science is now universally realised. All educated people are acquainted with the main scientific achievements of recent years, at least by name and nature if not more deeply. Thus relativity, the atom and the electron, and the spectra are terms familiar to many outside purely academic circles. The methods by which this knowledge has been attained are realised by comparatively few people.

The book gives a short and simple statement of the methods and results of modern physical and chemical science. It may serve both as an introduction to deeper study and as an account suitable for the general reader whose main intellectual interests lie in other fields of thought.

The first chapter professes to give an account of "matter." The author describes the persistence, conservation and transmutation of matter, but does not include a definition of the term. Other chapters deal with dynamics and the physical properties of matter, heat and energy, electricity and magnetism, chemical action and equilibrium, organic and biochemistry, radioactivity, atomic radiation and relativity and astro-physics.

Specialists will regard the treatment as brief, but it is nevertheless good. A slight typographical error has crept in on p. 21 (fifth line from the bottom). The atomic number of lead and radium D is 82, *not* 81, but this slip is, of course, of very minor importance.

It will be observed that a very wide field is surveyed within the covers of this work. In the section on organic chemistry a more modern type of combustion furnace than that on p. 152 might have been depicted, but in the main the book will serve a very useful purpose in bringing the scientific method to the notice of the general public.

Messrs. Doulton, of Lambeth, have issued a beautiful volume, entitled *The Royal Doulton Potteries*, which gives a brief summary of the rise and expansion of this well-known firm during six reigns. In addition, there are numerous reproductions of some of the artistic manufactures, photographs of the works, and of buildings in the construction of which Doulton wares played an important part. The reproductions in natural colours are especially noteworthy.

New Patents.

THIS list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

Latest Patent Applications.

16507—Burdick, J. N.—Process of making olefin oxides. July 9.

16704—Legeler, E.—Production of carbon disulphide. July 11.

16283—Pease & Partners, Ltd.—Recovery of pyridine, &c., from by-products. July 7.

16342—Spence & Sons, Ltd., P.—Production of ferric sulphate. July 8.

Specifications Published this Week.

217943.—Loftus, F. H.—Metallurgical furnaces.

217988—Stewart, R., and Laporte, Ltd., B.—Manufacture of barium peroxide.

218014—Soc. of Chemical Industry in Basle.—Manufacture of soluble acid calcium salts of inosite-phosphoric acid.

218053—South Metropolitan Gas Co., Evans, E. V., and Stanier, H.—Treating gases for removing carbon disulphide.

218119—Shimadzu, G.—Method of manufacturing powder of lead suboxide intermingled with powder of metallic lead.

218154—Walton, S. A., and Tokalon, Ltd.—Manufacture of oleo stearate of glyceryl.

218178—Lacy, S. A. de.—Frame to make possible the same apparatus, solvent recovery by distillation, after extraction of a substance has been made by that solvent.

209722—Wibaut, J. P.—Manufacture of alkyl-halides.

Abstract Published this Week.

216368—Ethyl chloride.—Farbwerke vorm, Meister, Lucius & Bruning, Hoechst-a-Main, Germany.

Ethyl chloride is prepared by the inter-action of ethylene or gases containing ethylene with hydrochloric acid gas in the presence of sulphur dioxide. The chloride of ethyl sulphurous acid is formed as an intermediate product. A catalyst, such as ordinary or activated charcoal, bauxite, burnt pyrites or terracotta, may be present, and increased pressure may be employed. Examples are given.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

THE CHEMICAL NEWS,

VOL. CXXIX. No. 3357.

THE MECHANISM OF PHOTOSYNTHESIS.

By Dr. Jaroslav Peklo.

The readiness with which carbonic acid can be reduced to formaldehyde is one of the most suggestive facts throwing light upon the mechanism of photosynthesis, and one that lends strong support to the *hypothesis that formaldehyde* is an intermediate product of photosynthesis. This, together with various biological observations, has led Willstätter to conclude that carbonic acid is rearranged by the absorption of light energy into a formaldehyde-peroxide complex from which, by means of an enzyme (catalase) action, formaldehyde is liberated, oxygen evolved, and chlorophyll regenerated. The scheme of the process, according to Willstätter,* would be as illustrated on page 92.

Some years before the war, in Pfeffer's laboratory, I conducted a series of experiments on the so-called "inactivation" of photosynthesis, in order to penetrate a little into the nature of its mechanism.

If assimilating plants are treated with certain concentrations of potassium cyanide, photosynthesis will be stopped for a time without any injury to the plant, which, after the poison is removed, will gradually recover, until its photosynthetic ratio is once more normal ("inactivation").

Having compared the effect of other poisons on the treated organisms, it was proved that potassium cyanide very likely inactivates quite different chemical processes, which consequently are to be considered as phases of photosynthesis. These experiments show that the same substances are actually present in the mechanism of photosynthesis as were postulated as active agents in Willstätter's scheme.

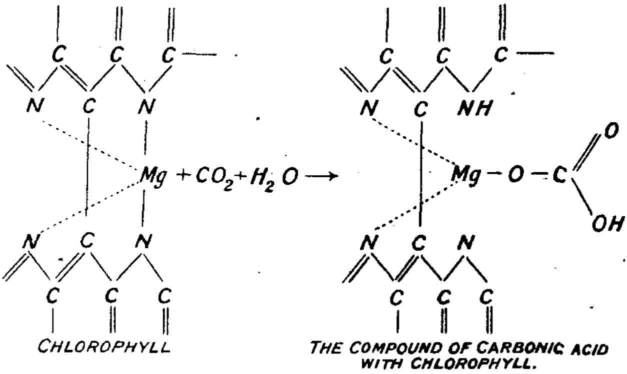
Limitations of space prevent me from describing more than the main results of my experiments.†

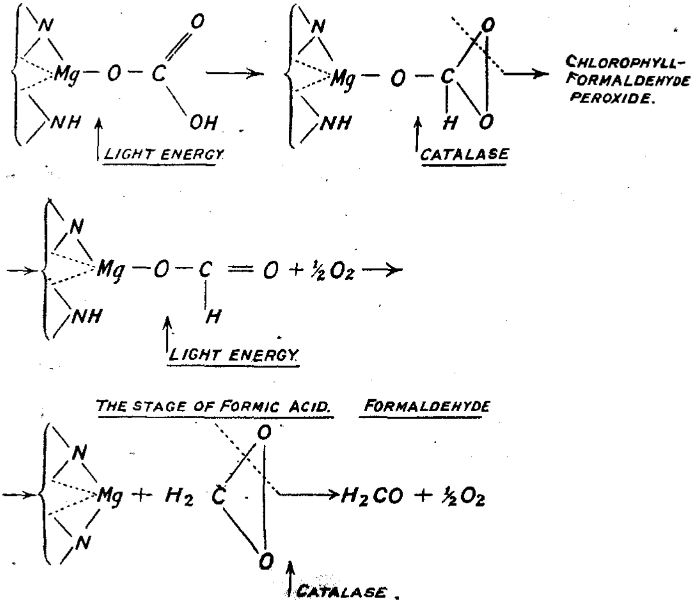
I applied the bubble-method; chiefly on *Elodea canadensis*, which in some series was succeeded by *Ceratophyllum submersum*, *Hottonia palustris*, *Ranunculus aquatilis* and *R. paucistamineus*, and *Potamogeton crispus*, *v. serratus*. The bubble-method has many disadvantages, which can be overcome if rich material reacting promptly and regularly is used, if the illumination and temperature are kept constant during the experiments, and if the physical and chemical properties of the water used in the experiments are precisely controlled. The CO_2 and O_2 contents of the water and their pressure must not be subject to change. In control experiments secondary reactions of the substances used to induce the "inactivation" must be eliminated, otherwise they would react either with the CO_2 contents of the water or with the oxygen liberated from the plant. For this reason, where the presence of oxygen was liable to disturb the result of the reaction, oxygen-free water was used, and the liberation of bubbles was induced by over-pressure of another gas. Quantitative estimates were made of the concentration of substances which showed change during the inactivation experiments. The courses of the reactions were controlled, when possible, by Engelmann's test with aerobic bacteria and delicate leaves of mosses. Attention was given also to shock-reactions of the plants treated. The obstruction of intercellular spaces during the experiments was prevented, the purity of the liberated gas was controlled, and care was taken that the solutions of poisons really penetrated into the plants. Certain water-plants showed a very specific reaction to potassium cyanide. If a certain quantity of this salt was placed in the assimilation water, or if a plant was immersed in a solution of the salt, the secretion of bubbles stopped immediately, and did not resume during the action of the salt. Provided the action did not last

*Willstätter and Stoll, *Untersuchungen über die Assimilation der Kohlensäure.* 1918.

† Described *in extenso* in the author's paper: *Studies on the Inactivation of Photosynthesis and on the Formation of Chlorophyll.* (Publications of the Bohemian Academy of Science, pp. 100, 1913, Prague, *in Bohemian*.)

1a)


Mg + CO2 + H2O →
Mg — O — C
OH
CHLOROPHYLL
THE COMPOUND OF CARBONIC ACID WITH CHLOROPHYLL.

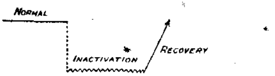

LIGHT ENERGY
CATALASE
CHLOROPHYLL-FORMALDEHYDE PEROXIDE.
= O + ½O2 →
LIGHT ENERGY
THE STAGE OF FORMIC ACID.
FORMALDEHYDE
Mg + H2
H2CO + ½O2
CATALASE.

too long, if the treated plant were transferred to normal water, *i.e.*, with the original CO_2 and O_2 tension, it recovered slowly. The bubbles began to develop and their number augmented until the original degree of assimilation was attained, the poison leaving no permanent trace of its influence. Consequently, the process is an inactivation, not a poisoning. *The quantity of potassium cyanide necessary* to induce inactivation was variable, the reaction of plants varying individually. With feebly assimilating plants in a faint light, 0.0025 per cent. KCN was sufficient. In artificial light (incandescent gas, and tantalum filament light of 100 candle power), 0.025 per cent. KCN and 0.011 per cent. HCN, to 0.056 per cent. KCN and 0.024 per cent. HCN. Far higher concentrations had to be *used in bright, diffused daylight. During* the month of May, on the continent, 0.088 per cent. KCN and 0.035 per cent. HCN were insufficient to cause complete stoppage of assimilation, and was only considerably weakened during 40 minutes' reaction. Photosynthesis in *Elodea* was only reduced to about one-fifth by 0.136 per cent. KCN and 0.056 per cent. HCN in 20 minutes, and in another case required 0.25 per cent. KCN and 0.106 per cent. HCN. In one case complete inactivation and full recovery succeeded in a solution of 0.456 per cent. KCN and 0.14 per cent. HCN. These concentrations were almost 10-20 times higher than those used with artificial light. It may be remembered that the *dosis letalis* for an adult man is ca. 0.15 g. KCN and 0.06 HCN.

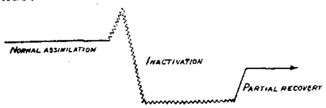
Recent literature has recorded no substance which would be so specific in its influence on the inactivation of the photosynthesis of water plants as KCN, *i.e.*, one which would inhibit the photosynthesis immediately, and after the plant was transferred to normal conditions would gradually recover.

Thus, various substances which I used as being characteristic of certain groups of chemical compounds showed very different effects: KCl and KNO_3, higher concentrations of which could influence photosynthesis through plasmolysis; NaF; phenol, which injured plants very quickly; aqueous solutions of chloroform, ether and chloral hydrate, which did not inactivate at all, but injured the assimilation in an irreversible manner; more vigorous and efficacious oxidising agents, $HgCl_2$, etc., reacted differently towards the plant than KCN and HCN.

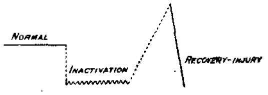
Formaldehyde showed a certain similarity in its effect to KCN, *i.e.*, it stopped assimilation and the plants recovered after its removal. There was, however, a significant difference. The effect of the KCN was to prevent the liberation of oxygen bubbles immediately, until the plant was removed from the action of the poison. From that moment its normal function recovered up to its former extent. The course of the KCN reaction can be illustrated diagrammatically as follows:—



The liberation of oxygen bubbles is suspended at the formaldehyde stage, for a certain time, before which the number of bubbles often increases. Complete recovery never occurs in normal water, and the diagram of the reaction can be written thus:—



SO_2 dissolved in water arrested the bubbles from the reductive substances (alkaline pyrogallol, hydrochinone). An increasing number of oxygen bubbles was shown at first in the period of recovery, probably in consequence of the additional effect of SO_2 in consuming the water-oxygen during the *inactivating time*. Later, however, the number of bubbles sank below the normal, and the plants showed an irreversible injury.



* A remarkable similarity came to light when the action of KCN was compared with the influence of solutions of H_2S and phenylhydrazine, $C_6H_5NH.NH_2$, on photosynthesis. The scheme was identical with that of KCN.

The supposed reaction of H_2S with the oxygen contents of the water was disproved by parallel experiments (the fall of the diffusion of oxygen through the surface of the plants was prevented). With the Engelmann's test an exact investigation was made of the oxygen output from the leaves of *Fontinalis antipyretica*, *Plagiotnecium denticulatum*, *Minum affine* and *Plagiochila*, *sp.*, and of its obstruction by solutions of H_2S and phenylhydrazine. These experiments showed that the reducers acted on the living cells. In the macroscopical experiments with phenylhydrazine its slow penetration in the tissues of *Elodea* disturbed the regular course of the reaction. On the contrary, the Engelmann test showed the smallest quantity of O_2 sufficient to induce the bacteria to move, even in the presence of the poison, and around air bubbles suspended in the preparation it could be seen how the movement was induced. It also permitted the observation as to how this movement was stopped in consequence of the arrested photosynthesis respectively of the stopping of O_2 exhalation from the leaflets during a stronger inactivation. Through the control of the oxidation processes in the H_2S solutions it was possible to state definitely that their influence was not external. The physiological effect of both the H_2S and the phenylhydrazine was established throughout the whole series of the experiments.

Cyanic acid is reputed to be an enzymatic poison, Κατεξοχήν, and it is doubtless an extraordinarily strong poison to catalases. It can also attack the zymase of alcoholic fermentation, but hydrolytic ferments (pepsin, proteolytic enzymes of *Nepenthes*, endotryptase of yeast cells, and diastase) resist it very strongly. These facts were used by Schroeder (1907) to explain the intensive inactivating action of KCN on the respiration of *Aspergillus niger*. He considered it an important fact that the enzymes which decompose hydrogen peroxide, and peroxydases (which are probably important for respiration), as well as zymase (respiration and alcoholic fermentations) are particularly strongly and transiently paralysed by this poison similarly to the respiration process itself; and that other enzymes are inactived only slightly, if at all, by HCN. Consequently he thought it not improbable that the same processes were the bases of the action of KCN on respiration as on the above-mentioned enzymes.

My experiments show, on the other hand, the efficacy of H_2S and phenylhydrazine, and show that their action is exactly parallel with that of KCN. H_2S and phenylhydrazine, although well known to have a paralysing action upon catalyses, have no effect upon other enzymes such as pepsin, trypsin, diastase and emulsin, which are also unaffected by KCN. These similarities are certainly very striking, and are made even more remarkable by consideration of Willstätter's scheme. According to this, the chlorophyll-formaldehyde-peroxide must be attacked by a catalase if oxygen as an assimilation secretion is to be liberated from assimilation.

The conclusions to be drawn from my experiments are therefore that the participation of some catalases in assimilation must be presumed, and that Willstätter's hypothesis is now proved.

Warburg, in a series of papers, has given the results of his investigations on the action of KCN on living cells, and on photosynthesis. He also imitated in models the physico-chemical processes of living cells. The superficial inactivation which HCN brought about with charcoal he explained as being its action on iron contained in the coal. My own conception of these processes is that considering the fact that iron shows a catalytic effect in the breaking up of H_2O_2, the question may be asked whether it does not have some similar effect on Willstätter's assimilation catalase.

The Institute for Applied Botany,
Bohemian Technical University,
Prague.

MARKET FOR DENTIFRICES IN NORWAY.

A short report on the market for toothpastes in Norway has been prepared in the Department of Overseas Trade from information forwarded from the office of the Commercial Secretary at Christiania. Firms interested in the exportation of British made dentifrices can obtain copies of the report upon application to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.

THE STRUCTURE OF CALCIUM.

By Hawksworth Collins, B.A. (Camb.).

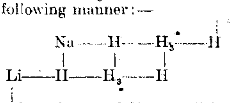
The only elements of atomic weight less than 60 from each of which a single electro-positive force is known to emanate are K(39), Na(23), Li(7), H_3(3), and H(1).

The atomic weight, 40, of Ca can be split up into as many parts, 39, 23, 7, 3, 1, as the element has valences:—40 = 39 + 1. If its atomic weight had been any number but 40 between 31 and 42 inclusive, it would have been impossible to split it up in this manner. Again, if its atomic weight had been any number but 40, from 25 upwards, it could not have been split up into two such portions, of which the second is the unit (*The Chemical News*, 1924, CXXIX., 47).

It is, of course, impossible to bring into this arrangement a free portion, H—H_3, so that by the law of the formation of non-metals, Ca cannot be a non-metal; and by the law of positive and negative valences its two valences must each be electro-positive.

Therefore the number 40 is peculiarly suitable for explaining the properties of the element.

All the above remarks suggest that an atom of calcium has been formed by the union of one of K with one of H; but from mineralogical facts it might just as well have been formed by the union of Si and C in the following manner:—



three of the valences of Si neutralising three of C, leaving two electro-positive forces as there is no free H—H_3, and some internal atomic bonds, which are not represented in the diagram, coming into play, which prevent the element from disintegrating.

By the Interrelationship of the Elements (*The Chemical News*, 1920, CXX., 169), KH is equivalent to SiC, the reason being evident from the diagram, where the top line is Si, the bottom C, the right is H, and the left K. K will be shown later to have been formed from AlC, as in the diagram.

This structure will now be proved to be true quite independently by means of the laws of relative volume and heat of formation.

Table I.

The Relative Volumes of Calcium.

Ca	=	K	+	H
13.25	=	7.49	+	5.76
Ca	=	Si	+	C
12.24	=	11.53	+	0.71
14.54	=	13.83	+	0.71
25.66				

Table II.

Experimental Data illustrating Table I.

		Relative Volume.	Theor. S.G. at 15° C.	Obs. S.G.	
(165)	CaO	13.25 + 4.45	3.164	3.161	Karsten
(166)	$CaCO_3$	13.25 + 8 + 7.53 + 2(2.51)	2.959	2.938	- 2.995 Breithaupt
(167)	$CaSO_4$	13.25 + 15.53 + 2(7.53 + 2.51)	2.784	2.759	- 2.884 Schroder
(168)	$CaSO_4$	13.25 + 15.53 + 7.53 + 3(2.51)	3.102	3.102	Filhol
(169)	CaH_2	13.25 + 2(5.76)	1.7	1.7	Kaye
(170)	CaS	12.24 + 15.53	2.59	2.58	Maskelyne
(171)	$Ca(NO_3)_2$	12.24 + 2(3.8 + 3 × 7.53)	2.52	2.504	18° Favre
(172)	$CaSi_2$	12.24 + 2(13.02)	2.508	2.5	Nostrand
(173)	$CaTiO_3$	12.24 + 21.99	3.973	3.974	20° Brun
(174)	$MgTiO_3$	8.71 + 21.99	3.91	3.91	Hautefeuille
(175)	$CaCl_2$	14.54 + 2(15.085)	2.483	2.480	Playfair
(176)	CaO	14.54 + 2.51	3.28	3.25	Brugelmann
				3.32	Levallois
(177)	Ca_3P_2	3(14.54) + 2 (14.56)	2.50	2.51	Nostrand
(178)	$CaBr_2$	14.54 + 2(23.09)	3.3	3.32	11° Bodeker
(179)	Ca	25.66	1.56	1.566	Matthiessen
				1.55	Jobin
(180)	RbI	26.57 + 32.77	3.57	3.567	Setterberg
				3.55	25°/4 Nostrand

11.53 and 13.83 were shown to be volumes of Si in *The Chemical News*, 1924, CXXIX., 48. 0.71 was shown to be the commonest volume of C in 1,400 molecules, diagrams of which were sent to the Nobel Institute in 1914. K(7.49) is a constituent part of Rb, for 26.57 = 2(9.54) + 7.49 = Na_2K = Rb (*The Chemical News*, 1914, CIX., 28; and 1920, CXXI., 157).

TABLE III.

	Heat of Formation of Ca.		Original Volume.		Rel. Vol. in combination at 15 ° C.		Change of Volume.
(a)	53376	= 120 × 11.12 × 40	25.66	=	14.54	+	11.12
(b)	59568	= 120 × 12.41 × 40	25.66	=	13.25	+	12.41
(c)	64420	= 120 × 13.42 × 40	25.66	=	12.24	+	13.42
(d)	aq. 73533	= 120 × 15.32 × 40	25.66	=	10.34	+	15.32

TABLE IV.
Experimental Data Illustrating Table III.

	Theoretical Heat of Formation.	Obs. H.F.	Corresponds in Table II. with No.
(a)	CaO 53376 + 96155 = 149531	151900	176
(b)	CaO 59568 + 71515 = 131083	131500	165
(c)	CaO 64420 + 96155 = 160575	160000 (*Chem. News*, 1920, CXXI., 250).	
(a)	$CaCl_2$ 53376 + 2(56786) = 166948	169900	175
(b)	$CaCO_3$ 59568 - 13886 + 32341 + 2(96155) = 270333	269100 270800	166
(c)	CaS 64420 + 30681 = 95101	94300	170
(b)	$CaSO_4$ 59568 + 0 + 2(32341 + 96155) = 316560	317400	167

In Table V. a series of values of H.F. in aqueous solution are given. Of course these cannot be supported by relative volume by means of specific gravity, but they evidently corroborate one another.

TABLE V.

Heat of Formation in Aqueous Solution.		Obs. H.F.
$CaCl_2$	73533 + 2(63870) = 201273	201300 Thomsen
KCl	37274 + 63870 = 101144	101170
$CaBr_2$	73533 + 2(52930) = 179393	179430 Thomsen
KBr	37274 + 52930 = 90204	90230
CaO	73533 + 96155 = 169688	170230
CaO	73533 + 71515 = 145048	145000 Thomsen
CaS	73533 + 36898 = 110431	110230
K_2S	2(37274) + 36898 = 111446	111290, 113500

The following remarks upon the four relative volumes of Ca apply equally to all other atomic volumes in this and other papers.

There are generally three, frequently four, and sometimes five absolutely independent reasons for each value given:—

(1) The volume 14.54 at 15° C. is found to exist in numerous compounds, of which only four are given in Table II. because scientists have no time to look into anything that is not short and explicit. All four theoretical results are easily within 1 per cent of the experimental. The same remarks apply to the other two combining volumes.

(2) The three combining volumes are all doubly confirmed by experimental data concerning heat of formation, (*a*) because they all give the same original volume, (*b*) because this original volume gives the correct S.G. of the uncombined element.

(3). Each one of the three combining volumes has a definite structural meaning (Table I.).

(4) Each one of the four volumes will be shown later to be a volume of Ca when it

forms a constituent part of other elements.

(5) In *The Chemical News*, 1923, CXXVI., 197, two of the combining volumes are shown to give theoretical results easily within 1 per cent. of the experimental under the law of magnetic rotation: The magnetic rotation of an electro-positive element, when in combination, is the product of half its atomic weight and the reciprocal of its relative volume.

NOTE ON REVERSAL BY HYDROGEN PEROXIDE, SODIUM ARSENITE, AND LIGHT.*

By W. Clark, Ph.D., M.Sc., A.I.C., F.R.P.S.

Reversal with hydrogen peroxide has been observed by a number of photographic workers. Luppo-Cramer's work (*Phot. Korr.*, 1902, 563) appears to indicate that reversal resulted from the prolonged action of acids on the plate, although nitric and citric acids destroyed the gelatine before reversal was noticed. Sodium arsenite (see Bancroft, *J. Phys. Chem.*, 1910, XIV., 292) and other compounds have been shown to behave like hydrogen peroxide in an analogous way to light. The action can be explained by assuming that developability is the result of chemical interaction with something at the grain surfaces, giving rise to nuclei for development.

It is, however, possible that dispersion or peptisation may play a part. Hydrogen peroxide can destroy the latent image, apparently owing to this cause.

The anthor exposed plates equally in pairs, fixed and washed them. One from each pair was then treated with hydrogen peroxide, or sodium arsenite, while the other was soaked in water. The plates were washed and developed in a physical developer (containing $AgNO_3$ and Na_2SO_3 and *p*-phenylene diamine).

The results showed that both agents exerted a destructive action on the reduction nuclei left after fixation. That the silver nuclei play some part is shown by the fact that most of the bubbles were evolved from the most exposed parts of the plates.

The conclusion is drawn that the actions of light and of peroxide and arsenite are fundamentally different in causing reversal. Reversal by fogging agents is probably due to peptisation of the latent image. The action of light is probably only to affect the latent image indirectly.

* Abstracted from *The Photographic Journal*, 1924, LXIV., 363-369.

GENERAL NOTES.

CANADA'S COAL RESOURCES.

Attention has been directed during the sessions of the First World Power Conference to the possibility that the coal resources of the British Empire may be exhausted within a few centuries. So far as Canada is concerned, such a contingency seems to be remote. For many years the Canadian Geological Survey has been investigating the coal fields of the Dominion, and it has been estimated that the reserve of coal amounts to more than 1,000,000,000,000 tons, largely lignite, but including over 250,000,000,000 tons of bituminous coals. Though the greater part of the various coal fields have been studied in a general way, yet their extent is so great that detailed investigations by the Geological Survey have been limited to a relatively small part of the whole. The great extent of the Canadian coal fields is apparent when it is realised that basins of coal-bearing strata extend almost continuously for a length of 700 miles within the eastern part of the Rocky Mountains and adjoining foothills. The coals of this region are largely bituminous or semi-anthracitic, and seams ten to fifteen feet in thickness are common. In addition, thousands of square miles of the prairie country of Alberta, Saskatchewan and Manitoba are underlain by strata holding workable seams of lignite and bituminous coals, and important coal fields occur in British Columbia, both in the interior and on the Pacific coast, while highly developed coal fields occur in the East in Nova Scotia and New Brunswick, in some cases at tide water.

THE POSITION OF CEREAL AND OTHER CROPS.

From information furnished in the International Crop Report of the International Institute of Agriculture, the position as regards the cereal crops may be summarised as follows:—

In the majority of the countries of Europe June was a month of changeable weather, with frequent downpours and occasional hailstorms which resulted in some local damage. On the whole it may he said that the current season has proved fairly favourable for the cereal crops. At the beginning of July, crop conditions were exceptionally

below those of a month earlier. Cereal prospects generally indicate an average yield, or even a trifle better, but they remain at a point well below that attained last season. In the main, it may be affirmed *that in Northern and North-western Europe* the yield will be somewhat over average, and quite good in Central Europe; while drought has reduced the crops below the average line in the South and South-east.

The French Colonies of North Africa and the grain-growing parts of Asia Minor also forecast poor yields owing to want of moisture. In Canada the area under wheat is 4 per cent. less than last year's, and the crop has been backward, but it was fairly promising at the beginning of July; at the fifteenth of the month the outlook remained good in Manitoba and fairly so in South Saskatchewan and South Alberta, but in the centre and north of these two provinces serious drought damage has occurred. The *official estimate of yield will appear next* month. In the United States the new crops promised, at the beginning of July, better results than were forecasted early in June, with the sole exception of maize. The most recent reports are more favourable for the cereal crops in general.

In the aggregate, the reports at present available seem to confirm the forecast, for the Northern Hemisphere, of smaller crops this year than last, in consequence of the reduction in areas sown in North America and of less favourable weather experienced this season in many countries.

As regards Southern Hemisphere prospects, information from Australia reports a sufficiency of rainfall; the outlook is consequently *favourable for the crops, but more* rain is required for maintaining this situation.

The data already to hand in regard to the 1924 crops indicate yields of 43.5 million metric tons of wheat, against 47.4 million last year; of 4.5 million metric tons of rye against 4.4 million; of 8.7 million metric tons of barley, against 10.0 million in 1923, and of 21.4 million metric tons of oats, as compared with 20.7 million last season.

It may be estimated that the countries whose figures are included in the totals represent, on the average, contributions of 65 per cent. of the wheat yield in the Northern Hemisphere (excluding Russia), of 25 per cent. of the rye, of 40 per cent. of the barley, and of 45 per cent. of the oat crop.

THE INCREASED AREA UNDER SUGAR BEET.

According to the data compiled by the International Institute of Agriculture and published in the July International Crop Report, the area under sugar beet this season has increased in Belgium, France, Italy, *the Netherlands, Poland and* Czecho-Slovakia. The aggregate increase in these six countries is about 20 per cent., as compared with last year, and 53 per cent. when compared with the average of the previous five years. In Russia, too, there has been a decided extension of area under sugar beet, the actual increase over last year being about 40 per cent. The crop condition in Russia at the beginning of July was generally above average and decidedly better than at the same period of last season. In North America the area has also been increased; the crop condition is similar to last year's in Canada, but is somewhat lower in the United States.

THE INCREASED AREA UNDER FLAX.

The International Institute of Agriculture states that from the data already to hand there is shown an increase in area in Belgium, France and the Netherlands; while the area is much the same as last year in Italy, Lithuania and Czecho-Slovakia. A large addition to area sown has been effected in Canada and the United States, amounting respectively to 21 per cent. and 64 per cent. as compared with last year.

The prospects are generally good, but in Ireland the flax crop is very late and a small yield is expected; while in Western Belgium there are complaints of much laying of the growing crop.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE CHEMICAL SOCIETY OF JAPAN.

Papers communicated:—

On the Natural Soaps in Soy Bean, by SHUNSUKE MURAMATSU.

Studies on Sulphide Acids. Part I. Butyl Ether of Thioglycolic Acid, by E. EMMET REID and YOSHISUKE UYEDA.

Studies on Sulphide Acids. Part II. Isobutyl Ether of Thioglycolic Acid, by YOSHISUKE UYEDA and JINZO KAMON.

Studies on the Insecticidal Principle in CHRYSANTHEMUM CINERARIAEFOLIUM. *Part IV. Insecticidal Principle Produced on Dry Distillation of* CHRYSANTHEMUM CINERARIAEFOLIUM, by RYO YAMAMOTO and MIZUTO SUMI.

ROYAL AGRICULTURAL SOCIETY.

The proceedings at the Monthly Council, on July 30, included the presenting of the report of the Chemical Committee:

Mr. Luddington (Chairman) reported that the list of analyses made by the Consulting Chemist for members during the months of June and July had been submitted. Further consideration had been given to the Report of Departmental Committee on the Fertilisers and Feeding Stuffs Act, 1906, referred back to them by the Council of June 4. After discussion it had been resolved:—

"That the Chemical Committee, having carefully considered the Report of the Departmental Committee on the Fertilisers and Feeding Stuffs Act, 1906, without committing itself to points of detail, gives a general approval of the proposals of the Departmental Committee, and, feeling that these constitute a great advance in the right direction on the present administration of the Act, urges the Ministry of Agricultnre to take immediate action in bringing in a new Act on the lines indicated in the Report of the Departmental Committee."

The Consulting Chemist had submitted the material which he had prepared for inclusion in "Occasional Notes." This consisted of a summary of the recommendations of the Departmental Committee on the Fertilisers and Feeding Stuffs Act, and particulars of several cases which had already been before the Chemical Committee. This had been passed subject to the approval of the Chairman.

Various matters arising out of his correspondence had been submitted to the Committee by Dr. Voelcker.

In moving the adoption of this report, Mr. Luddington pointed out that the Committee had slightly modified the terms of the recommendation to the Council regarding the report of the Departmental Committee on the Fertilisers and Feeding Stuffs Act. At the same time, they felt that it was very essential that some indication should be given to the Ministry of Agriculture on the matter. The Departmental Committee had been set up largely at the request of the Council, and because they all felt that it was very necessary to have some alteration of the existing Act. The Committee felt that a Bill introduced on the lines of the recommendations contained in the report would be a great improvement. Of course, they reserved to themselves full powers to criticise any sections of a Bill that might be brought forward. They felt it would be a distinct advantage to agriculturists that a Bill should be brought in forthwith on the general lines of the recommendations of the Departmental Committee.

Mr. Christopher Middleton said he would like to second the adoption of the Committee's report, and desired to add a few words in support of what had been said by the Chairman. It was very desirable that the Society should give a lead to other agricultural bodies in the country on the question of this report. It was quite true that they had not got everything for which they had asked; but he had himself given evidence before the Departmental Committee, and he must confess that a great many of the points to which they attached importance had been met. There was, however, one question, the removal of the veto of the Ministry of Agriculture, which had not been secured, but a considerable compromise had been made regarding that. The veto was not absolutely abolished, but a distinction was made in the Committee's recommendations between criminal and civil proceedings. For a vendor not give an invoice, it was to be a criminal offence, and it was left to a local authority to institute proceedings. The only reservation was that in criminal proceedings for misrepresentation the sanction of the Ministry had to be obtained. He thought it was a great advance on the previous Act, and for that reason he hoped the Council would give the report a general approval. He not say that they should commit themselves to all its details, but they should give a lead to agricultural opinion on this matter; and he hoped the Council would unanimously adopt the recommendation of the Chemical Committee.

The Chemical Committee's report was then adopted.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

[TORONTO MEETING.]

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCE.

(*Continued from Page* 89.)

PROF. J. C. MCLENNAN, F.R.S.—*Recent Developments in Low Temperature Research.*

MR. F. J. W. WHIPPLE.—*The Diurnal Variation of Pressure: Facts and Theories.*

PROF. W. J. HUMPHREYS.—*The Relation of Wind to Height.*

On the average, perhaps, and especially on the equatorial side of cyclones, the wind varies as follows with height: Increases rapidly, but decreasingly so, with height up to 400 to 500 metres above the surface; then decreases slightly through, say, 300 metres; after this increases a little, and then remains, roughly, constant up to round 2,000 to 3,000 metres above the surface; here again often slightly decreases; and then through the next several kilometres increases in proportion to decrease of density. Directions of the wind and its temperature also are interestingly related to height above the surface.

All these observed facts are plausibly explained as effects of mechanical and thermal turbulence.

MR. J. BJERKNES.—*The Importance of Atmospheric Discontinuities for Practical and Theoretical Weather Forecasting.*

MR. L. F. RICHARDSON. — *Turbulence and Temperature-Gradient among Trees.*

DR. H. JEFFREYS.—*Tidal Friction.*

PROF. W. L. BRAGG, F.R.S.—*The Relation between Crystal Structure and Refractive Index.*

When an electromagnetic wave passes through a medium the electric field polarises the atoms, their positive and negative components being displaced from the normal configuration. This creates a field around each atom equivalent to that of an electric doublet whose moment is proportional to the electric vector at each instant. The velocity of the wave in the crystal depends on the ratio between the total polarisation per unit volume and the field.

Each atom is affected by the general field and by its polarised neighbours. In a crystal which has been analysed by X-rays the effect of neighbouring atoms on each other can be calculated. The double refraction of Calcite and Aragonite, for instance, can be satisfactorily explained quantitatively. This holds for other crystals, and similar calculations are of interest when applied to gases.

It appears probable that a better measure of atomic refractivity will be arrived at when due allowance is made for atomic arrangement.

PROF. C. H. DESCH, F.R.S.—*The Crystal Surface.*

The atoms in a crystal being arranged on a space lattice, all atoms in the interior of the crystal must be held in position by forces symmetrically disposed. At the surface of the crystal this symmetry disappears, so that the surface layer of a crystal must possess properties different from those of the mass. A part of this difference manifests itself as surface tension. With increase of temperature, the cohesion and the surface tension in general diminish, but not necessarily at the same rate. At high temperatures, the surface tension may be sufficient to cause rounding of the sharp angles of a crystal. This is shown by experiments with gold. Beads of gold, slowly cooled from the liquid state, have a skin which has properties like those of a film of gelatin, the normal structure being exposed when the film is removed by etching. The sharp octahedral "etch-figures" on large crystals of gold, or the angles of minute crystals prepared by precipitation, become rounded at temperatures several hundred degrees below melting-point. Other effects of surface tension in solid metals are given.

DR. G. SHEARER.—*The Chemical and Physical Significance of X-ray Measurements of Compounds containing Long Chains of Carbon Atoms.*

Such measurements appear to give reliable values for the lengths of these molecules; they show that the basis of the structure is actually a chain of carbon atoms which may have one or other of a limited number of forms. The observed rates of increase of the lengths of the molecules with the number of carbon atoms

they contain are in accordance with the assumption that successive pairs of carbons are linked together at the tetrahedral angle; this would imply a marked directive property of the valency bond in carbon. The method of investigation would appear capable of throwing light on many problems of stereochemistry—geometrical isomerism, the nature of double and triple bonds, &c. The existence of spacings often as great as 60 A.U. makes is possible to observe a large number of successive orders of reflection, and a study of the intensity distribution among these different orders is of interest.

PROF. W. L. BRAGG, F.R.S., and PROF. S. CHAPMAN, F.R.S.—*A Theoretical Calculation of the Rhombohedral Angle of Calcite.*

The paper describes an attempt to calculate theoretically the rhombohedral angle, or axial ratio, of crystals of the calcite type. A number of carbonates form rhombohedral crystals similar to calcite, which can be referred to three equal axes. The angle between the axes is in the neighbourhood of 102° for the whole series.

There must be some fundamental reason for the occurrence of this angle throughout the series. The crystals consist of ions R^{++} and CO_3^{--}, where R may be Mg, Ca, Mn, Fe, Co, Ni, Zn, Cd. One can picture the rhombohedral crystal symmetrically extended or compressed along a trigonal axis, keeping constant the distance between neighbouring oxygen and metal centres, and neighbouring carbon and oxygen centres. The electrostatic potential energy per gram-molecule has been calculated for a series of such positions, and it has been found that it has a minimum value in the neighbourhood of 106°. Taking into account the approximate nature of the assumptions on which the calculation is based, this may be regarded as in satisfactory agreement with the observed value of 102°. Further it is possible to calculate the effect on the rhombohedral angle of substituting other metal ions for calcium, and it has been found that the slight variation in angle, which is 101° 55′ in $CaCO_3$ and 103° 2′ in $MgCO_3$, is accurately explained.

MR. W. T. ASTBURY.—*The ... tion of Molecular Symmetry and its Possibilities as a Method of Deriving Structural Formulæ.*

Given the class of any crystal, we can, with two exceptions, decide definitely the space-group, and thence, from the number of molecules per cell, derive the only symmetry elements possible to the molecules as they are built into the crystal. Then, by a critical examination of the dimensions of the cell and the relative positions of the molecules within it as given by the space-group, it is often possible to make a clear choice between two or more suggested structural formulæ, even though the molecule be fairly complex. But, in general, it is essential to know from chemistry the various possibilities. The molecular symmetry in the crystal is in general less than what would be expected of a molecule in the free state. A brief account will be given of the application of this method to the problem of the isotrimorphism of the tervalent metallic acetylacetones and the structure of the acetylacetone group.

MR. S. H. PIPER. — *X-ray Crystallographic Methods as an Aid to Chemical Research.*

PROF. W. L. BRAGG, F.R.S.—*Exhibit of Models illustrating Crystal Structure.*

DR. J. S. OWENS.—*The Automatic Measurement of Atmospheric Pollution.*

MR. J. PATTERSON.—*Upper Air Observations in Canada.*

PROF. H. H. KIMBALL.—*The Determination of Daylight Intensity from Automatic Records of Total Solar and Sky Radiation.*

PROF. W. J. HUMPHREYS.—*Rainmaking.*

PROF. C. F. MARVIN.—*Let us Simplify the Calendar and Publish Statistical Data in Standardised Summaries.*

PROF. V. BJERKNES.—*The Forces which Lift Aeroplanes.*

DISCUSSION on *The Scattering of light.*

PROF. R. W. WOOD, FOR. MEM. R.S.

PROF. C. V. RAMAN, F.R.S.—*The Scattering of Light in Relation to the State of Molecular Aggregation.*

B. KENRICK.—*Light-Scattering ... Salt Solutions.*

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The light-scattering and depolarisation factor have been measured for aqueous salt solutions prepared dust-free by the method of envelopment. The intensities of scattering are compared with the calculated values.

PROF. W. H. MARTIN.—*The Relation between the Depolarisation Factor of the Scattered Light and the Electrical Double-Refraction in Liquids.*

Richard Gans' theory of the relation between the depolarisation factor of the scattered light and the Kerr constant of electrical double-refraction in liquids is submitted to experimental test for some fifteen liquids. Measurements of the depolarisation factor for nitrobenzene made in a magnetic field of 5,000 gauss failed to show any change in the polarisation of the scattered light.

MR. R. MELDRUM STEWART and MR. J. P. HENDERSON.—*Wireless Time Signals.*

REV. A. L. CORTIE.—*The Relation between Solar Activity and Terrestrial Magnetic Disturbance.*

MR. E. A. HODGSON.—*Correlation of Records of two Distant Milne-Shaw Seismographs.*

MR. J. J. SHAW.—*Report of the Seismology Committee.*

PROF. SIR ERNEST RUTHERFORD, F.R.S. —*Lecture on Atomic Disintegration.*

PROF. A. S. EDDINGTON, F.R.S.—*Theory of the Outflow of Radiation from a Star.*

MR. E. A. MILNE.—*Radiation Pressure and the Equilibrium of the Solar Chromosphere.*

DR. L. SILBERSTEIN.—*Determination of the Curvature Radius of Space-Time.*

DR. H. H. PLASKETT.—*The Spectra of Nebulæ.*

The paper discusses some new observations on the spectra of nebulæ. These new observations furnish the absolute intensities of the hydrogen and some "nebulium" lines as determined by the wedge method in the Orion Nebula, partially confirm the previous interferometer results in assigning a low atomic weight to "nebulium," and finally contain a complete description of the new gaseous envelope star Z Andromedæ, discovered at Victoria. In the discussion these and the much more numerous earlier observations are treated in an attempt to determine (*a*) the mode of excitation of the nebular radiation, and (*b*) the nature of the carrier of the "nebulium" spectrum, in particular if it is a H He molecule.

MR. J. JACKSON.—*Photographic Proper Motions of Faint Stars.*

DR. R. K. YOUNG and DR. W. E. HARPER. —*Methods and Results of Spectroscopic Absolute Magnitude Determinations.*

DR. F. HENAOTEAU.—*The System of σ Scorpii.*

SECTION B.—CHEMISTRY.

PRESIDENTIAL ADDRESS, by SIR ROBERT ROBERTSON, F.R.S., on *Chemistry and the State.*

PROF. W. A. BONE, F.R.S.—*The Activation of Nitrogen in the Explosion of Carbon Monoxide-Air Mixtures at High Initial Pressures.*

The paper describes the principal experimental results obtained by the author in conjunction with Messrs. D. M. Newitt and D. T. A. Townend during the recent researches upon gaseous combustion at high pressures, in which it has been discovered that nitrogen exerts a peculiar energy-absorbing influence when carbon monoxide-air mixtures are exploded in a bomb at high initial pressures, which is not manifest at all when corresponding hydrogen-air mixtures are similarly exploded. The observed facts are explained on the supposition that there is some constitutional correspondence between CO and N_2 molecules (where densities are identical) whereby the vibrational energy (radiation) emitted when the one burns is of such a quality as can be readily absorbed by the other, the two thus acting in resonance. The nitrogen thus becomes chemically "activated" in carbon monoxide-air explosions at high initial pressures, and in such state is able to combine with oxygen more readily than does nitrogen which has merely been raised to a correspondingly high temperature in a hydrogen-air explosion. The influence of varying initial ex-

plosion pressures up to 100 atmospheres upon the said "nitrogen-activation" is shown, and the bearing of the results upon the problem of "nitrogen-fixation" discussed.

PROF. JAMES KENDALL and MR. BEVERLEY L. CLARKE. — *A New Method for the Separation of Elements of the Rare Earths.*

The ionic migration method previously proposed for the separation of isotopes (*Proc. Nat. Acad. Sci.*, 1923, IX., 75) has been successfully extended to the fractionation of certain rare earth mixtures. A gel containing the given mixture is placed in a long glass tube, between a section of KCl gel (nearer the anode), and a section of chromic sulphate gel (nearer the cathode). On electrolysis, since the K^+ moves more rapidly than the rare earth ions, and the Cr^{+++} moves more slowly, the two boundaries of the central section remain quite sharp even after it has travelled a long distance. If the rare earth ions themselves have appreciably different mobilities, the faster ion should accumulate in the front portion and the slower in the rear portion of this section, so that a complete separation should readily be obtained. Short runs have been carried out with three mixtures—yttrium-erbium, gadolinium-samarium, and neodymium-praseodymium. In the first two cases a 400-c. run gave practically perfect separation; in the last the separation was only partial.

DR. F. W. ATACK.—*Isomerism of Oximes.*

PROF. J. F. SNELL.—*Malic Acid from Maple Sugar Sand.*

MR. D. A. PRITCHARD.—*The Canadian Salt Company's Processes for the Manufacture of Alkali-Chlorine Products.*

The plant of the Canadian Salt Company at Windsor, Ontario, is situated over salt deposits of vast extent, and is near enough to Niagara Falls to render the use of electric power from that source economical. The plant is also favourably located for both water and rail distribution. The first electrolytic alkali plant in Canada was installed in 1912 by this company. Details are given of the construction (illustrated by lantern slides) of the electrolytic cell used and of its operation, efficiency, &c. The cell is named after its inventor, Arthur E. Gibbs, an Englishman. In Canada, the United States, and England there have been installed to date Gibbs' cells to the capacity of approximately 45,000 h.p. Details are given of the mechanical bleach-making equipment employed, believed to be the only successful one on this continent. A complete description of the manufacture and handling of liquid chlorine, in which industry the company is the pioneer in Canada, is also given.

MR. R. L. PEEK.—*The Electro-Refining of Nickel.*

(Followed by General Discussion on Canadian Electrochemical Industries, Prof. F. G. Donnan, F.R.S., Mr. H. Freeman, Mr. F. A. Sidbury, and Mr. F. A. J. Fitz-Gerald taking part.)

(*To be continued.*)

NOTICES OF BOOKS.

Chemical Thermodynamics, by J. R. PARTINGTON, D.Sc. Pp. VI. + 275. London: Constable & Co., Ltd., 10-12, Orange Street, W.C.2. 1924. 10s. 6d. net.

This important contribution to the literature of physical chemistry is really a successor to the author's "Text-book of Thermodynamics with special reference to Chemistry," which appeared in 1913.

The first chapter deals in detail with specific and latent heats, and is followed by an account of the first law of thermodynamics. A brief chapter on thermochemistry is concerned particularly with Hess's law, and Kirchhoff's equation has been inserted before a discussion on the second law. The ideal gas, the changes of physical state, the characteristic equation, dilute solutions, and entropy are all considered in adequate detail.

Later chapters are concerned with further applications of thermodynamical principles. Useful lists of symbols and of abbreviations have been appended.

Examples are given at the end of each chapter, the answers being given at the end of the book. The treatment is thorough, and assumes a good acquaintance on the part of the student with general chemistry, physics and mathematics. Much recent work, especially American, has been made use of.

The Vacuum, by J. A. Cochrane, B.Sc. Pp. VI. + 103. London: G. Bell & Sons, Ltd., York House, Portugal St., W.C.2. 1924. 1s. 6d.

The cultivation of pseudo-science must be guarded against, but, on the other hand, the inculcating of scientific principles is much more important than acquiring a mere list of facts, however striking these may be.

Mr. Cochrane is therefore to be congratulated for writing this simple yet scientifically accurate book on the vacuum and that which appertains to it.

After giving an account of the early (Aristotelian) notions such as that "*Nature abhors a Vacuum,*" the author goes on to instance cases where nature seems to prefer a vacuum. Modern ideas, as a consequence of wider experience, indicate that the universe is mainly void—a vacuum between the stars and planets.

The experiments of Galileo, Torricelli, Pascal, and Perier, which culminated in the construction of the barometer, are described in an interesting manner.

A chapter is devoted to the invention of the air-pump, and reference is made to Guericke's Magdeburg hemispheres. This is followed by a more detailed account of the pressure of the air. Methods of demonstrating the weight and pressure of air are cited. This pressure is shown to be exerted equally in all directions.

The modern suction,* double-barrel, sprengel and water-jet pumps are all minutely described. The author does not omit to mention the methods of measuring a vacuum and its properties. Finally, the every-day uses and applications of the vacuum, such as in the making of thermos flasks, X-ray bulbs and wireless valves, show how important an understanding of these phenomena can be.

In an excellent, if brief, introduction, Mr. E. J. Holmyard, the general editor of this remarkably cheap series of books on the *Phenomena of Nature*, points out that for the majority of people science should be an outlook upon nature rather than a smattering of technical information. Mr. Cochrane has indeed written a very fascinating little volume on the vacuum, that is, on *nothing*! It is well illustrated, and should appeal equally to young readers and to adults who have lost touch with scientific thought, and who find it hard to gather up the threads again from more ponderous and abstruse tomes. J.G.F.D.

Nitroglycerin und Nitroglycerinsprengstoffe (Dynamite). von Dr. Naoum. Pp. XI. + 416. Berlin: Julius Springer, Linkstr. 23. 1924. $4.30.

Nitroglycerin, or more correctly, glycerin trinitrate, is obtained by the interaction of one molecule of glycerin with three of nitric acid, water being eliminated and absorbed by a dehydrating agent:—

$$\begin{array}{l} CH_2\,OH \\ | \\ CH\;\;OH \\ | \\ CH_2\,OH \end{array} + 3HNO_3 = 3H_2O + \begin{array}{l} CH_2\,ONO_2 \\ | \\ CH\;\;ONO_2 \\ | \\ CH_2\,ONO_2 \end{array}$$

Mono- and di-nitroglycerins are also formed to a slight extent during this reaction.

Nitroglycerin, the basis of dynamite, is perhaps the most important explosive known, but the mono- and di-nitroglycerins (α and β forms of each are known), in which one or two of the hydroxyl groups of the trihydric alcohol have been replaced, are of no importance for explosive purposes.

The present volume, the chief feature of which is perhaps its extreme German thoroughness, deals in detail with the preparation and manufacture of nitroglycerin and the explosives derived from it.

In addition to the specifications which the starting products must show, the author has included descriptions of the preparation and properties of homologous nitric esters. There is also an appendix on the chemical analysis of explosives containing nitroglycerin.

For future editions the author might note that Pressburg is now in Czecho-Slovakia, and not Hungary (p. 9).

The volume should prove of value to chemists and others engaged in the production of explosives. J.G.F.D.

First (Experimental) Report to the Atmospheric Corrosion Research Committee (of the British Non-Ferrous Metals Research Association), by W. H. J. Vernon, B.Sc. Pp. 839 to 934. March, 1924. The Faraday Society. 7s. 6d.

This Report on the atmospheric corrosion of non-ferrous metals gives an account of the systematic investigation of the action of the atmosphere upon metals and typical alloys, from the earliest stages.

The enormously greater attack of iron than of other metals is brought out, and although this side of the subject is only inci-

dentally touched upon, its practical value is obvious.

The detailed study has indicated for the first time the marked difference in the mechanism of corrosion with different metals. This discovery promises to prove of the greatest importance, both from a practical point of view as well as in leading to a further elucidation of the whole question of corrosion.

The work was commenced in 1921, and consequently the specimens used have not yet reached an advanced state of corrosion, and the report is mainly concerned with the phenomena of tarnishing, rather than actual corrosion.

Three different types of tarnishing have been distinguished. In the first type, represented by copper, the tarnish film actually protects the metal from further attack, the progress of tarnishing becoming slower and slower as exposure proceeds. This is accounted for by the supposed continuous layer which the tarnish film forms, and the consequent difficulty the corroding constituents of the air find in reading the underlying metal.

In a second type the tarnish is neutral, and the attack proceeds steadily. Finally, corrosion may become accelerated, and forms the third type exemplified by iron, as the product, rust, assists in the attack.

Some metals, such as zinc, brass, etc., may follow more than one type of progress, according to the atmospheric conditions, or even to the thickness of the tarnish film. For instance, with brass the attack first proceeds uniformly, but later the film exhibits a protective influence, and the attack slows off.

M.r Vernon has also investigated other apparently quite distinct types of film which form upon certain metals when exposed to the air. Nickel and some of its alloys at first seem not to tarnish at all, but rather to condense or produce on the surface a fog or cloudiness, which can be readily removed by simple washing with alcohol, restoring the bright metallic surface underneath.

The discussion on the paper, which is appended, has emphasised the importance of a detailed laboratory study of the tarnish films themselves. The future seems to demand a greater knowledge of the constitution and life-history both of desirable and undesirable films.

The Faraday Society is to be congratulated upon issuing this work as a separate volume. The importance of the subject is well recognised, and has previously been referred to in *The Chemical News*, 1923, CXXVII., 388, 395, and this vol., p. 10, at the time of its presentation last December.

New Patents.

This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

Latest Patent Applications.

16886—Clark, G. M.—Manufacture of double compounds of dimethylxanthines, earth alkali and salicylic acid. July 14.

16920—National Aniline & Chemical Co., Inc.—Production of o-nitranisole. July 15.

17025—Williams, J. G., and Millar, J. T.—Preparation of water-soluble phosphate salts. July 16.

17203—Naamlooze Vennootschap Philips' Gloeilampenfabrieken.—Separating hafnium and zirconium. July 17.

17061—Technical Research Works, Ltd.—Production of metallic catalysts. July 16.

Specifications Published this Week.

218347—Worsley, A. — Production of hyposulphurous acid and the use thereof.

218354—South Metropolitan Gas Co., Woodall, Duckham, & Jones (1920), Ltd., and Hatfield, H. S. — Electrostatic separation of particles.

199354—Naugatuck Chemical Co.—Processes for the manufacture of diphenylguanidine.

218414—Walker, H. V.—Nitration of cellulose.

218458—Green, A. G., Oxley, H. F., and British Dyestuffs Corporation, Ltd.—Separating alkylamines from ammonia and other gases.

199721—Pereira, H.—Process of manufacturing amino-perylene-quinones.

218542—Cassella & Co., Ges. L.—Production of acridinium compounds.

Abstract Published this Week.

216461—Treating copper compounds.—Edwards, G. W., and Durant, H. T., 3, East India Avenue, London.

Roasting.—Ores or other materials containing copper in the oxidised condition, including oxides, hydroxides, carbonates, silicates, basic, or oxychlorides, &c., such as malachite, azurite, chrysocolla and atacamite, are mixed with a solid carbonaceous material and heated at a temperature of 300-550° C. in an oxidising atmosphere, after which the product is amenable to an ammoniacal leaching process, such as that described in Specification 215802. The ore, &c., is crushed to a fine state of division, for example, to a linear mesh of 30, and is mixed either before or during crushing with coal, coke, charcoal, sawdust, straw, hay, or manure, &c., and is charged into a reverberatory furnace, where it is heated with an excess of oxygen for about an hour, during which time it is agitated by rabbling, &c. After discharge from the furnace the product is allowed to cool and recrushed, if necessary, before being submitted to the leaching process.

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THE CHEMICAL NEWS,

VOL. CXXIX. No. 3358.

THE STRUCTURE OF COBALT

By Hawksworth Collins, B.A. (Camb.).

In *The Chemical News*, 1920, CXXI., 182, five main principles in the constitution and structure of the chemical elements were given, and in accordance with these the constitution of cobalt was shown to be AlS.

This deduction will now be proved to be correct quite independently by means of the laws of relative volume and of heat of formation.

TABLE I.

The Relative Volumes of Cobalt.

Co	=	Al	+	S
6.78	=	3.74	+	3.04
11.56	=	4.05	+	7.51
14.56	=	4.05	+	10.51
4.05	=	4.05	+	0

TABLE II.

Experimental Data Illustrating Table I.

	Relative Volumes.	Theor S.G. 15° C.	Obs. S.G.	
(181)	Co 6.78	8.702	8.71	Lampadius
			8.558	Henry
(182)	CoF_2 11.56 + 2(5.42)	4.33	4.43	Nostrand
(183)	$CoCl_2$ 11.56 + 2(15.085)	3.115	2.937	Playfair & J.
			3.348	25°/4 Nostrand
(184)	$Co(ClO_4)_2 + 7H_2O$ 11.56 + 2(38.07) + 7(14.03)	2.07	2.075	International
(185)	$LiClO_4$ 5.46 + 38.07	2.446	2.428	25°/4 International, *i.e.*, 2.448 15°
(186)	Co_2O_3 2(11.56) +2 (4.45) + 2.51	4.81	4.814	Playfair & J.
(187)	$CoCl_2 + 6H_2O$ 14.56 + 2(15.085) + 6(14.03)	1.846	1.84	13° Bodeker
(188)	$CoSO_4 + 7H_2O$ 14.56 + 30.59 + 7(14.03)	1.960	1.964	15°.5 Pettersson
			1.958	15°.6 Pettersson
(189)	$Tl_2Co(SO_4)_2 + 6H_2O$ 2(22.29) + 14.56 + 2(30.59) + 6(14.03)	3.75	3.729	16° Pettersson
			3.768	15° Pettersson
(190)	$CoSiF_6 + 6\frac{1}{2}H_2O$ 14.56 + 13.02 + 6(5.42) + $6\frac{1}{2}$(14.03)	2.074	2.067	Topsoe
(191)	$Li_2SiF_6 + 2H_2O$ 2(5.46) + 13.02 + 6(5.42) + 2(14.03)	2.27	2.338	Stolba
			2.244	Topsoe
(192)	$CoCl_3 + 6NH_3$ 4.05 + 3(15.085) + 6(18.11)	1.7	1.704	Jaeger
(193)	$CoCl_3 + 5NH_3$ 4.05 + 3(15.085) + 5(18.11)	1.8	1.802	15° Jorgensen
(194)	$CoCl_3 + 4NH_3 + H_2O$ 4.05 + 3(15.085) + 4(18.11) + 14.03	1.85	1.847	Jaeger
(195)	Mo = Na_3Al 9.44 = 3(1.9) + 3.74	10.17	10.02	- 10.32 Int.
(196)	MoC 9.44 + 3.44	8.4	8.4	20° Nostrand
(197)	C (diamond) 3.44	3.49	3.492	Grailich

TABLE III.

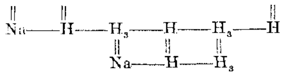
Heat of Formation of Cobalt.	Original Volume.		Rel. Vol. in combination at 15° C.		Change of Volume.
- 33842 = 120 × (-4.74) × 59					
aq. - 32920	6.78	=	11.56	-	4.78

TABLE IV.

Experimental Data Illustrating Table III.

	Theor.	Obs	
H.F. solid CoF_2 - 33842 + 2(76820) =	119798	120300	(corresponds with No. 182)
H.F. aq. CoF_2 - 32920 + 2(77500)	122080	122200	
H.F. solid CaF_2 64420 + 2(76820)	218060	218400	216450
H.F. aq. FeF_2 - 27790 + 2(77500)	127210	127000	
H.F. aq. $CoCl_2$ - 32920 + 2(63870)	94820	95040	94820 Thomsen
H.F. aq. $SrCl_2$ 67950 + 2(63870)	195690	195690	Thomsen
H.F. solid CoSe - 33842 + 46380	12538	13900	pp.
		9900	cryst.
H.F. aq. $CoBr_2$ - 32920 + 2(52930)	72940	72940	Thomsen
H.F. aq. $SrBr_2$ 67950 + 2(52930)	173810	173810	Thomsen
H.F. aq. CoI_2 - 32920 + 2(37720)	42520	42520	Thomsen
		40700	
H.F. aq. NaI 32706 + 37720	70426	70300	Thomsen
H.F. aq. SrI_2 67950 + 2(37720)	143390	143460	Thomsen
H.F. aq. FeI_2 - 27790 + 2(37720)	47650	47650	Thomsen

The above experimental facts demonstrate that Al + S is the correct constitution for Co, and that its structure is



showing that it can act either as a dyad or a triad, but not as a non-metal.

The volume, 3.74, for Al in Table I., is supported exactly by the constitution of Mo given in No. 195, Table II., and will be shown later to be a constituent part of other elements.

In the paper on Selenium (*The Chemical News*, 1924, CXXVIII., 408), it was stated that 1.9 and 5.76 would appear as volumes of Na in other elements. Both these values have now been confirmed, the former here, and the latter in the paper on Silicon.

The volumes 7.51 and 10.51 for sulphur were given in *The Chemical News*, 1924, CXXVIII., 289 and 408.

The volume 11.56 for Co takes the place of 11.45 (*The Chemical News*, 1922, CXXV., 82), and there is a corresponding small change in its H.F. solid.

The volume 3.04 for sulphur will appear later as a constituent part of silver. The only remark that can be made at present with regard to it is that the two volumes of Ag given in the paper on bismuth differ by 3.04.

SUMMARY.

The constitution of an atom of cobalt, which had been previously given in *The Chemical News* as AlS, is here proved to be correct; and at the same time the four laws, given in full in the paper on silicon,* are strengthened; also the demonstration of Specific Gravity as an exact instrument of research is extended.

There are no hypotheses either in this or in other papers, but the whole is simply a demonstration of truths which underlie experimental data.

THE INFLUENCE OF LIGHT ON AQUEOUS SOLUTIONS OF POTASSIUM IODIDE, NITRATE AND CHLORATE.*

BY K. SURYANARAYANA.

In view of the great many conflicting statements found in chemical literature regarding the influence of light on aqueous solutions of potassium iodide in the presence and absence of acids, mineral and organic, and on account of the important role which aqueous solutions of potassium iodide play in iodometry, it was thought worth while by the author to verify some of the statements and work out in a reproducible

* *Reprinted from "The Journal of the Science Association," Maharajah's College, Vizianagaram, 1924, II., 12.*

way the conditions in which potassium iodide solutions are effected by tropical sunlight.

The experiments of Ernest Cook are the most comprehensive regarding the influence of light on aqueous potassium iodide solutions in the presence and absence of acids. As has been remarked by Mellor[1], in many of the investigations concerning the topic in hand, the "authors" did not take the precaution of employing pure potassium iodide, free from iodate, and consequently many of the conclusions are unreliable.

In the following series of experiments, potassium iodide of Kahlbaum reduced by means of zinc-copper couple and crystallised from absolute alcohol was employed. The acids employed were tenth normal solutions of pure hydrochloric, sulphuric, acetic, oxalic, and tartaric acids. Aqueous solutions of pure potassium iodide were placed in test tubes along with the acids and were exposed to diffused and direct sunlight, starch emulsion being added previously. In every case, the familiar starch blue colour made its appearance after some time, direct sun light producing quicker results than diffused light. The speed of appearance of blue colour is also dependent on the strength of the acid, the order hydrochloric, sulphuric, oxalic, tartaric and acetic acids being one of decreasing speed. The same solutions placed in complete darkness did still show decomposition of potassium iodide only considerably more slowly than in diffused daylight.

The next series of experiments was calculated to eliminate the part which air plays in the decomposition. In different limbs of an apparatus, specially constructed for the purpose, the iodide solution with some starch emulsion and the acid solution were placed. The solutions were vigorously boiled to free them from dissolved air. While the solutions were boiling, pure nitrogen, tested to be free from oxygen and carbon dioxide, was passed through the apparatus and the glass nozzles communicating with the outside were sealed by means of a blow-pipe flame. The solutions were then mixed by opening the stopcock separating the two limbs containing the solutions and tilting the apparatus gently. The mixture so formed was exposed to direct sunlight for two to three hours, but no trace of the blue colour appeared. Subsequent admission of air into the apparatus caused the appearance of the familiar blue colour. Experiments were conducted with success, using the weaker carbonic acid instead of the stronger acids. Thus it is clear that a conjunction of any acid, even a weak acid like carbonic acid, and oxygen, is necessary *for any visible decomposition of potassium* iodide in solution to take place. With a view to find out if light of shorter wavelengths has any influence on the decomposition of acidified potassium iodide, when oxygen is completely excluded, the experiments were repeated with quartz test tubes as containers for the solutions and light from an iron arc instead of direct sunlight. The experiments ended in a failure. Thus it is clear that the presence of oxygen is essential for the decomposition of acidified solutions of potassium iodide, irrespective of the nature of the light to which the system is exposed. By the joint action of light and oxygen on acidified solutions of potassium iodide, the oxidation proceeds slowly in the beginning till a small amount of iodine is liberated, when the change proceeds with increasing velocity until the latter becomes constant. This is probably due to the auto-sensitising action of the liberated iodine. But as iodine accumulates in quantity, the velocity of the reaction gradually falls to a minimum, due to the fact that iodine in solution acts as a light filter.

In this series of experiments an interesting side observation was made with regard to the photolytic decomposition of some oxysalts like potassium chlorate and potassium nitrate, etc. When a solution of pure potassium iodide and the oxysalt was confined in a quartz test tube rigidly excluding carbon dioxide and oxygen from the system and exposed to ultraviolet light, there was always an unmistakable evidence of the decomposition of potassium iodide, perhaps due to the liberation of oxygen in a very active state as a result of the photolytic decomposition of the oxysalt. It is remarkable that the oxysalt should under the influence of ultraviolet light decompose furnishing the necessary oxygen for the oxidation of potassium iodide.

When neutral solutions of these oxysalts were individually exposed to the action of ultraviolet light, without the addition of potassium iodide, evidence of their decom-

[1] *A comprehensive treatise of inorganic and theoretical chemistry*, 1922, II., 607.

position was easily obtained by analysing the solutions qualitatively for the decomposition products; for potassium nitrite could always be recognised in the exposed potassium nitrate solution by means of Peter Greiss reaction and chloride in the case of potassium chlorate by means of silver nitrate. Direct sunlight causes photolysis in the solutions of these oxysalts. In the case of sodium nitrate E. Laurent (*Bull. Acad. Belgique*, 1891, (3) 21, 337) observed that a solution of it is decomposed in sunlight with evolution of oxygen.

It was found that after a small fraction of the oxysalt is decomposed, a 'steady state' is established. Thus in the case of potassium nitrate it was observed that the decomposition $KNO_3 \rightarrow KNO_2 + O$ can be inhibited by the addition of a large excess of KNO_2. Again, it was observed that in the case of a solution of the oxysalt which was left unstirred during the course of exposure to light, the equilibrium between the nitrate and the nitrite is dependent upon the thickness of the solution and its concentration.

SUMMARY.

1. A solution of potassium iodide when contaminated with oxygen and even a weak acid like carbonic acid liberates iodine even in the dark. When the decomposition proceeds in light the iodine liberated has an autosensitising action on the velocity of the decomposition. If oxygen is rigorously excluded from the system no decomposition of potassium iodide occurs, even when the system is exposed to ultraviolet light. The velocity of the decomposition when once started is associated with the intensity of light and on the hydrogenion concentration of the acid associated with the solution of potassium iodide.

2. Ultraviolet light induces decomposition in solutions of oxysalts like potassium nitrate and chlorate with the liberation of oxygen, and the formation of nitrite and chloride and the reactions are reversible.

3. After a small fraction of potassium nitrate is decomposed a steady state is established. Potassium nitrite is found to inhibit its decomposition if added in a large quantity.

4. The equilibrium between potassium nitrate and nitrate depends upon the concentration and thickness of the solution of nitrate when the solution is not stirred during exposure to light.

In conclusion, the author wishes to take this opportunity of thanking Professor Y. Venkatramaiah for his kind and helpjful interest in the work while working in the Research Laboratories, H.H. The Maharajah's College, Vizianagaram, during the summer vacation of 1923.

PACHAIYAPPA'S COLLEGE,
MADRAS.

PROCEEDINGS AND NOTICES OF SOCIETIES.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

[TORONTO MEETING.]

SECTION B.—CHEMISTRY.

(*Concluded from Page* 103.)

JOINT DISCUSSION with Section C, on *Liquid and Powdered Fuels.*

(*a*) DR. G. S. HUME.—*Liquid Fuels in Canada.*

The production of oil in 1923 in Canada was obtained from wells in New Brunswick, Ontaria, and Alberta, but was only 1.3 per cent. of the total consumption of crude and refined oils for the same time, representing an adverse trade balance of nearly 31½ million dollars. Such a condition has greatly stimulated boring operations within the last few years, and tests of prospective fields have been made in many places, the most promising results being obtained in Alberta. However, even though a certain increase in production is possible from wells, the consumption is so far in excess of production that the probabilities of making Canada independent of foreign oil supply in the near future from this source alone are not very great. Canada, however, possesses immense potential resources of oil in the tar sands of Alberta and the oil shales of the Maritime Provinces. The tar sands of Alberta occur over an area of 7,500 to 8,000 square miles, some portions of which give 20 per cent. bitumen carrying an oil content as high as 69 per cent. The oil shales of New Brunswick and Nova Scotia will in places produce as much as 30 to 36 imp.

gals. of oil to the ton with some by-products, and the amount of oil shales available is exceedingly large. For neither of these deposits, though, has a satisactory commercial process of extraction been evolved up to the present, although the technical difficulties are being studied by experimental work and laboratory investigation, and it is hoped a solution will be discovered.

In Nova Scotia, in 1915, the Dominion Iron and Steel Co. began the recovery of benzol and toluol with other products from the coking of coal. These were used during the war for the manufacture of explosives, but subsequently have been combined as a motor fuel, the production of which reached 292,000 gals. in 1921. It is claimed that this motor fuel possesses qualities which make it superior to the best gasoline, and with the establishment of coke ovens elsewhere in Canada, such as are now under consideration, motor fuel from this source will become increasingly important.

(b) PROF. GEORGE A. GUESS.—*Pulverised Coal in some Metallurgical Plants.*

In reverberatory smelting pulverised coal was used successfully for the first time at the plant of the International Nickel Company at Copper Cliff, Ontario, in 1914. The difficulties that had to be overcome in the use o pulverised coal in reverberatory work are described and the advantages attendant upon its use are indicated. The experience of certain smelting works with powdered coal is given, and the use of the same for steam-raising is touched upon.

(c) PROF. W. A. BONE, F.R.S.—*Brown Coals and Lignites.*

The paper discusses (*a*) the classification of sub-bituminous coals generally, with special reference to brown coals and lignites, and (*b*) their occurrence and distribution throughout the British Empire. Attention is directed to their economic importance, and to the need of more co-ordinated research and investigation into their properties and uses with a view to developing within the Empire a scientific brown-coal technology. Some results of the author's recent investigations upon the drying, heat treatment, and carbonisation, &c., of brown coals are described from the point of view of their bearing upon the many problems which their utilisation presents to the fuel technologist.

PROF. J. W. MCBAIN, F.R.S.—(1) *The Conception and Properties of the Electrical Double Layer and its Relation to Ionic Migration.* (2) *The Rate of Saponification of Oils and Fats by Alkali.* (3) *Limitations to the Use of Indicators in Alkaline Solutions and in the Presence of Soaps.* (4) *The States of Matter exemplified by Soaps and their Solutions.*

(1) *The Conception and Properties of the Electrical Double Layer and its Relation to Ionic Migration.*

Our present knowledge of the double layer between liquids and such materials as glass, membranes, and colloidal particles is reviewed, and the numerous and conflicting assumptions which have been put forward in calculating the "contact potential" are stated explicitly. It is emphasised that the contact potentials currently employed have a fictitious significance, and it is therefore urged that experimental results be recorded in the form in which they are observed—namely, movement in an electric field or electromotive force set up by bodily movement.

A conception of the double layer with sparsely distributed mobile ions is developed which appears to harmonise the existing data, including also those for absolute electrode potentials and for the behaviour of sols, gels, and curds of soap (cf. earlier paper by Miss Laing). If this conception is a true interpretation of the existing data, the fundamental assumptions made in all previous mathematical treatment of this subject are invalid.

(2) *The Rate of Saponification of Oils and Fats by Alkali.*

It has been ound possible to measure the rate of saponification of oils by means of a hydrogen electrode at 90°, and to isolate the various factors involved. The rate depends, for example, upon the amount of emulsified oil, and it is found that even with vigorous stirring only a limited proportion of the oil present is truly emulsified. Excellent monomolecular constants are obtained for the dependence of the rate on the hydroxyl ion present.

(3) *Limitations to the Use of Indicators in Alkaline Solutions and in the Presence of Soaps.*

Most of the commercial indicators have been tested at 18° and 90° in solutions of

pure sodium hydroxide, and serious discrepancies are found in results with Sörensen's standard buffer solutions and with pure hydroxide, most of the indicators giving quite misleading and useless results. Two, or possibly three, indicators can be used in the presence of soaps, and under suitable conditions confirm measurements of the hydrolysis of soaps obtained by other methods.

(4) *The States of Matter exemplified by Soaps and their Solutions.*

Soaps form an almost unique material for the precise investigation of the relations between a number of interesting states of matter. Any one aqueous soap can be prepared in the form of true hexagonal crystal lamellæ: white, opaque (crystalline) curd fibres, transparent liquid crystals (conic anisotropic liquids), and transparent isotropic solutions which are dark when examined with crossed Nicols. The isotropic solutions are crystalloids or colloidal electrolytes, and the latter are either fluids or true jellies depending in a most regular manner upon temperature and concentration. A mass of quantitative data is now available for each of these states, and some insight has been obtained into their constitution and relationships.

PROF. WILDER D. BANCROFT.—*The Permeability of Membranes.*

PROF. H. S. TAYLOR.—*The Adsorption from Silver Salt Solutions by Silver Iodide.*

PROF. W. LASH MILLER.—*The Distribution of Colloidal Gold between Two Liquid Phases.*

PROF. E. F. BURTON.—*The Mutual Action of Electrically Charged Particles in Solution.*

This paper deals with the mutual effect of particles in suspension in liquids due to their possession of an electrical charge.

Continuing experiments first performed many years ago by Dorn, Billiter,* and Freundlich, small spheres of metal have been dropped through columns of various liquids and quantitative measurements made of the charges carried down by these spheres. It is observed that a scattering of the particles takes place which is undoubtedly influenced to a great extent by the charges borne by the particles.

PROF. P. J. MOLONEY.—*The Absorption of Insulin by Charcoal.*

PROF. FRANK B. KENDRICK.—*Traces of Colloids in Distilled Water.*

A discussion of the source and removal of motes in distilled water used for light-scattering measurements, and of the part these motes play in the prevention of the supersaturation of gases.

SECTION C.—GEOLOGY.

PROF. A. P. COLEMAN, F.R.S.—*The Pleistocene Rocks of the Toronto Region.*

PROF. W. A. PARKS.—*The Palæozoic Strata at Toronto.*

DEAN G. F. KAY.—*Some Recent Interpretations of Glacial Deposits in Iowa.*

PROF. W. A. PARKS.—*The Dinosaurs of Alberta.*

DR. F. A. BATHER, F.R.S.—*The Habits of some North American Cystids.*

PRESIDENTIAL ADDRESS by PROF. W. W. WATTS, F.R.S., on *Geology in the Service of Man.*

PROF. E. S. MOORE.—*The Direction of Cleat in Coal.*

PROF. M. B. BAKER. — *Metallogenesis and the Pre-Cambrian of Canada.*

ASSOCIATE-PROF. ALEXANDER MACLEAN. —*The Structural Features of the Kirkland Lake Gold District.*

DR. J. M. BELL and ASST.-PROF. ELLIS THOMPSON.—*The Effect of Deep-seated Alterations upon the Mineralogical and Geological Features of the Keeley Mine.*

DR. L. J. SPENCER, F.R — *International Agreement in Mineralogical and Crystallographical Nomenclature.*

PROF. REGINALD A. DALY.—*The Earth's Elastic and Non-Elastic Deformation, caused by the Waxing and Waning of Ice-caps.*

PROF. W. M. DAVIS.—*Modification of Darwin's Theory of Coral Reefs by the Glacial-control Theory.*

PROF. A. P. COLEMAN, F.R.S.—*Raised Beaches as Related to the Thickness of Ice Sheets.*

PROF. W. M. DAVIS.—*An Uptilted and Bevelled-off Atöll.*

PROF. J. W. RUSSELL.—*Evidences of a quite recent Extinction of the American Mastodon.*

DR. W. G. MILLER.—*The Pre-Cambrian Rocks of Canada.*

DR. M. E. WILSON.—*The Grenville Pre-Cambrian Sub-province.*

PROF. T. T. QUIRKE.—*Correlation of the Huronian and Grenville Rocks of South-Eastern Ontario.*

MR. H. C. COOKE.—*Folding and Mountain-building in the Pre-Cambrian of Northern Ontario and Quebec.*

PROF. R. C. WALLACE.—*Some Types of Mineralisation in the Pre-Cambrian Rocks.*

DR. ELLSWORTH.—*Radio-active Minerals in Pre-Cambrian Strata.*

PROF. A. P. COLEMAN, F.R.S.—*Pre-Cambrian Climates.*

MR. EDWARD M. KINDLE.—*Certain Types of Sedimentation now in Progress on or near the Atlaitic Coast of North Amerca.*

DR. C. A. MATLEY.—*Recent Geological Work in Jamaica.*

DR. C. A. MATLEY.—*A Reconnaissance Geological Survey of the Cayman Islands, British West Indies.*

PROF. O. T. JONES.—*The Ordovician-Silurian Boundary in Britain and North America.*

PROF. O. T. JONES.—*The Llandovery Rocks of Llandovery.*

MR. G. ANDREW.—*The Llandovery Rocks west of Builth, Breconshire.*

MR. GEORGE SLATER.—*Glacial Tectonics as Reflected in Drift Deposits.*

SECTION D.—ZOOLOGY.

MR. F. A. POTTS.—*Intracellular Digestion in Invertebrates.*

MR. D. WARD CUTLER and MISS L. M. CRUMP.—*Observations on the Growth and Reproduction Rate of a Ciliate.*

PROF. A. F. COVENTRY.—*Modifications of Heart Development in the Perch.*

PROF. A. BROOKER KLUGH.—*The Effect of Temperature on the Rate of Reproduction in Cladocera.*

PROF. W. M. TATTERSALL and MISS E. M. SHEPPARD.—*Sex Phases in the Female of Asellus aquaticus (Linn.).*

MR. J. S. HUXLEY.—*Linkage in Gammarus chevreuxi.*

DR. F. A. E. CREW.—*Studies in the Sexual Differentiation of the Fowl.*

DR. J. W. HESLOP HARRISON.—*On Hybrids between British and Canadian Lepidoptera.*

MR. A. D. PEACOCK.—*Sexuality in the Saw-fly (Pristiphora pallipes, Lep.): a Study in the Evolution of Parthenogenesis.*

DR. F. A. DIXEY, F.R.S.—*On Scent-distributing Structures in the Lepidoptera.*

PROF A. E. CAMERON.—*Some Tabanidæ of Saskatchewan, their Parasites and hitherto undescribed pre-imaginal and imaginal Stages.*

JOINT DISCUSSION with Section M (*q.v.*) on *Soil Population.*

MISS K. E. CARPENTER.—*On the Biological Factors involved in the destruction of River-Fisheries by Pollution consequent on Lead-mining.*

MR. E. MELVILLE DU PORTE.—*Some Endophytic Protozoa. A contribution to our knowledge of the Protozoa living in the latex of plants.*

PROF. E. M. WALKER and MISS NORMA FORD.—*Some Features in the Anatomy of Grylloblatta, a primitive Orthopteroid Insect.*

PROF. J. W. MAVOR.—*The Effect of X-rays upon the Transmission of Mendelian Characters.*

SIR WILLIAM HERDMAN, F.R.S.—*Note on the Structure and Affinities of Ramulina.*

PRESIDENTIAL ADDRESS, by PROF. J. W. GAMBLE, F.R.S., on *Construction and Control in Animal Life.* Followed by discussion.

MR. J. T. CUNNINGHAM.—*Lamarckism and Secondary Sexual Characters.*

PROF. D. M. S. WATSON, F.R.S.—*Palæontology and Mendelism.*

DR. E. H. CRAIGIE.—*Changes in Vascularity in the Brain between Birth and Maturity.*

MR. J. M. SWAINE.—*The Factors determining the Distribution of North-American Bark-beetles.*

JOINT DISCUSSION with Section K (*q.v.*) on *Chromosomes and Species.*

PROF. E. E. PRINCE.—*Biological Board and Marine Research Stations of Canada.*

PROF. A. G. HUNTSMAN.—*The Circulation of the Water off the Canadian Atlantic Coast.*

PROF. A. G. HUNTSMAN.—*Certain Limiting Factors in the Distribution of Marine Animals.*

PROF. W. A. CLEMENS.—*Limnobiological Investigations in Ontario in Relation to Fishery Problems.*

MR. W. J. K. HARKNESS.—*Determination of the Rate of Growth and Age of Sexual Maturity in the Sturgeon (Acipenser rubicundus).*

PROF. W. J. DAKIN and MRS. C. M. G. DAKIN.—*The Physiology of Nutrition in Aquatic Animals.*

MRS. KATHLEEN F. PINHEY.—*Acartia clausi var. hudsonica nov. var. A contribution towards the Correlation of the Pelagic Copepod Coastal Fauna of Northern Europe and North America.*

MISS CATHERINE HERDMAN.—*Variation in Shore-Living Dinoflagellata.*

DISCUSSION on *The Origin of Land Vertebrates.* Opened by PROF. E. S. GOODRICH; PROF. D. M. S. WATSON following.

MR. A. WILLEY.—*Pterygopoda and Tetrapoda.*

PROF. W. K. GREGORY and MR. M. HELLMAN.—*The Dentition of Dryopithecus and the Origin of Man.*

DR. NELLIE B. EALES.—*The Anatomy of a Fœtal Elephant.*

THE BRITISH ASSOCIATION.

[TORONTO MEETING.]

PRESIDENTIAL ADDRESS TO Section B, by SIR ROBERT ROBERTSON, F.R.S., entitled *Chemistry and the State.*

It should be premised that in this account of the relationship of the State to chemistry in Great Britain, an attempt has been made to limit it to a description of the more or less direct assistance given by that science to various departments as they came into being or took form. Only in recent years, and as a result of the war, has there been a direct recognition of a corresponding obligation on the other side.

It is obvious that it is to the universities, and, as was the case to a greater extent in the past, to private workers, that the great advances made by British chemists are due. Departmental requirements have, of course, reaped the advantage of these advances, but examples of important contributions to chemical knowledge emanating from the departments themselves are not lacking. The collected story of their connection with the activities of the State may be worth reciting, if it should show the development of its appeal to chemistry, and illustrate the gradual breakdown of the view held by the chief of the tribunal before which Lavoisier came, that 'the State has no need for chemists.'

We will find that their employment in an official capacity was in the first instance in connection with the State's pressing necessities, such as its defence, the regulation of

its currency, and the collection of its revenue, all of them subjects warranting the maintenance of equipment and staff.

As the need for safeguarding the nation's health, well-being, and the quality of its food-supply became recognised, legislation followed, frequently based on the work of Commissions on which sat distinguished chemists of the day, and it became necessary to set up a State chemical department to assist in carrying this into effect.

For some time the science of chemistry had received a limited and vicarious assistance from State grants to the late Science and Art Department and to the universities, but it was reserved for the war to establish definitely and finally the position that the whole future existence of a State might and probably would depend on the existence of a flourishing and efficient chemical industry. This resulted in the definite steps of assisting the application of science to industry, and providing direct encouragement for workers in the purely academic field.

It is proposed, therefore, to sketch the development of the main chemical activities of the State, and to review the conditions in Great Britain in the hope that it may be of use generally to define the present position, and perhaps of interest to this Dominion in the present stage of its chemical development.

DEFENCE.—EXPLOSIVES.

It would appear that the importation of the technical process from abroad is no new thing, for it is stated that in 1314 gunpowder and guns were being imported into England from Ghent. Not only the material but the executant also appears to have been imported in the person of a John Crab, a Fleming, who took service with the English and supervised the guns and munitions used at Crécy. By 1338, cannon were mounted on board English ships of war, and in 1346 gunpowder was being supplied to the King. Although the manufacture of gunpowder is mainly a mechanical operation, variations in the composition which must have involved chemical experiment are recorded in such works as the 'Fire Work Books' of that interesting class, the Master Gunners. In England, a Master of the Ordnance in 1447 is stated to have made 20 tons of gunpowder. This manufacture, however, early became stabilised, and the proportions of the composition underwent little change until the middle of the nineteenth century, when it was modified, but as freedom from smoke began to be demanded a new propellant of a type that could be produced only by chemists was evolved.

It is of interest that Faraday was employed by the War Office as Lecturer at the Royal Military Academy from 1829 to 1853, and on appointment took as his assistant James Marsh, whose name, associated with the process for determining arsenic, is so well known to chemists. Marsh received the gold medal of the Society of Arts for this work, and a silver medal from the Board of Ordnance for his discovery of the quill percussion tube for cannon, and further he devised some of the earlier types of time-fuze. Abel succeeded Faraday at the Academy and began his long career of activity as scientific adviser to the War Office, becoming War Department Chemist in 1854.

It is necessary to mention some of the important advances made by Abel and his staff, including Kellner and Deering. By pulping guncotton, he rendered it safe to handle and store; his researches on the properties of guncotton laid the foundation of later work on its stability and explosive properties; and his research (with Noble) on the behaviour of gunpowder when fired is an example of a thorough investigation. Abel was consulted also on subjects other than explosives, and in his laboratory were conducted experiments which led to the adoption in 1879 of the present close-test apparatus for testing the inflammability of oils, experiments on steels and the effect of foreign materials in them, experiments on dangerous dusts and on the cause of accidents in coal mines.

The work of Abel in rescuing nitrocellulose from the position of an erratic substance, liable to decompose and explode on storage, led to its use as a reliable explosive, not only for military purposes, but also in commercial compositions, such as sporting powders and blasting explosives.

When it became necessary to devise a smokeless propellant for the British Service, the chemical work was in the hands of Abel with his assistant Kellner, Dewar, and Dupré, and in 1890 this resulted in the recommendation for the adoption of cordite.

It now became necessary to extend the

only chemical manufacture carried on at the Royal Gunpowder Factory, that of guncotton, by adding the manufacture of nitroglycerine, the technical handling of cordite, and plant for treating acids, and accordingly in 1891 a chemical manager of this section with a staff of chemists was appointed.

The chemical work carried out by the British Government for defence, both as to its immediate object and as to its reaction on the explosives industry of the country, is worth review. In such a review the position before the war may first be described. Propellant manufacture was seriously undertaken, the small quantity of high explosive used at this time being mostly obtained from private manufacturers. Guncotton, as has been stated, had been manufactured by Abel in a fairly stable form, and this explosive was chosen for the Service propellant cordite, together with nitroglycerine and mineral jelly, the mixture being gelatinised by acetone, so that in a plastic condition it might be squirted into the cords which give it its name. A close study was devoted to this manufacture in all its aspects; the processes of manufacture were greatly improved, and the dangers reduced.

The Royal Gunpowder Factory took its place as a model of an explosives factory, and afforded an example of what could be done by a State department in conducting a scientific manufacture with regard to improved technique, economy, and efficiency. Thus the method of nitration to produce guucotton was greatly improved in safety, freedom from fumes, and ultimate stability of the product, by the adoption of the process of downward displacement of the waste acids from the nitrated product by a layer of water; for nitroglycerine a displacement process by which the layer of that liquid, separating on the surface of the waste acids, was caused to overflow from the top of the vessel by introducing waste acid from a previous charge at the bottom, led to an increased safety and yield, and saved height in the erection of a factory; the chemistry of the process of guncotton boiling was worked out and placed on a scientific foundation; and acetone, which in the process of drying the cordite had been allowed to escape into the air, was recovered from the drying stoves and saved for further use. These advances in manufacturing method were taken up by other manufacturers, both in the United Kingdom and abroad.

In the technique of the manufacture of propellant explosives before the war this country then had advanced to a high pitch of efficiency, so that when the demand came for enormously increased quantities of propellants, new factories, such as that of Gretna, took up the manufacture on lines already well established.

Safety in manufacture had also been closely studied, and precautions introduced that commended themselves to private firms. It may be said in this connection that the application of the Explosives Act of 1875 by the Home Office Inspectors of Explosives has been of much benefit to the explosives trade in reducing casualties. Perhaps in no other country are precautions taken to such an extent as in Great Britain, so that to visitors from abroad they sometimes appear unnecessary and vexatious, but experience has shown that the policy is sound, especially as it brings into all sections of the work an atmosphere of carefulness and responsibility, with an eventual gain in health of the workmen and freedom from accidents.

Research on explosives before the war was carried out at the Royal Gunpowder Factory and at the Research Department, Woolwich. At the former establishment, the chemistry of the products manufactured was investigated, especially with regard to the mode of decomposition of guncotton, of nitroglycerine, and of cordite; their respective rates of decomposition at different temperatures were determined, a subject bearing on their behaviour on storage. Knowledge of this kind is essential in a Service such as ours, on account of the extremes of temperature from tropical to frigid to which explosives may be subjected in stations throughout the Empire.

At Woolwich an experimental establishment had been set up on the instigation of Lord Haldane to deal with explosives and metals used in gunnery. Here the study of the chemical and explosive properties of all types of explosives was undertaken and methods were developed for determining their stability and sensitiveness. This knowledge found application in laying down

criteria for the choice of explosives for use in a Service whose demands are exigent on account of the drastic conditions above mentioned, affecting both storage and the design of mechanism containing explosives. So far as the subject-matter is not considered to be confidential, this work has been published in scientific journals, so that it is available in connection with the study of the theory of explosive substances.

(*To be continued.*)

THE CHEMICAL SOCIETY OF JAPAN.

Papers communicated:—

On Amino-Acids Containing Sulphur. Part I., A New Method for the Determination of Cystein, by YUZURU OKUDA.

On Amino-Acids Containing Sulphur. Part II., A New Method for the Determination of Cystine, by YUZURU OKUDA.

On the Chemical Constituents of ASTRAGALUS SINICUS, L., by KIYOHISA YOSHIMURA and SHIRO FUJISE.

On the Nitrogenous Compounds in Oil Cake of BRASSICA CAMPESTRIS, *var.* CHINENSIS, *T. Ito*, by KIYOHISA YOSHIMURA and SHIRO FUJISE.

On the Nitrogenous Compounds in Pumpkin and Cucumber, by KIYOHISA YOSHIMURA and KOTARO NISHIDA.

On the Chemical Constituents of Tomato. Part I, by KIYOHISA YOSHIMURA and KOTARO NISHIDA.

On the Action of Sulphuric Acid upon a-Pinene, by KASHICHI ONO.

Uses of Amalgams in Volumetric Analyses. Part X., Estimation of Phosphoric Acid with Uranyl Salts, by SEIISHIRO SAITO.

GENERAL NOTES.

PRODUCTION OF ASBESTOS IN CANADA, 1923.

The Dominion Bureau of Statistics has just issued the following finally revised statistics on the production of asbestos in Canada during 1923:—

From the point of volume of sales, 1923 may be considered the premier year for the asbestos industry in Canada, but the total sales value of this commodity declined very materially. The sales for the year totalled 231,482 tons, with a return to the operators of 7,522,506 dollars, as compared with 163,706 tons sold in 1922 worth 5,552,723 dollars.

The total quantity of asbestos rock mined during the year amounted to 3,768,542 tons, of which 3,217,580 tons or 85 per cent. was milled. The mill recovery of marketable asbestos was 7.3 per cent. or 237,000 tons.

A small test shipment of crude No. 1 and 2 was made from a newly developed deposit of asbestos, near McKay Lake, Deloro Township, Ontario. In Quebec experimental operations were carried on by one firm to recover the fibre from asbestos rock by the wet process.

CORRESPONDENCE.

OVERVOLTAGE AND MELTING POINTS.

To the Editor of THE CHEMICAL NEWS.

SIR,—In reply to Prof. Partington's criticism of my paper on Overvoltage and Physical Properties (*The Chemical News*, 1924, CXXIX., 17), I should like to point out that my first general conclusion in my paper was that the metals may be conveniently divided into two groups: those with high melting points and low overvoltages, and those with low melting points and high overvoltage. Prof. Partington's table shows exactly the same relationship, the bridge being at antimony. Further, then, I pointed out in my table, as a general rule, but by no means an "approximately exact relation," that the higher the melting point of a metal the lower was its overvoltage.

In order to compare the results with those of Mott, melting points previous to 1911 were chosen, and were taken in general from Roscoe and Schorlemmer's Chemistry.

Since the paper was published, further research work by Sand and Weeks, which is in course of preparation for publication, has made a modification of my views on the

relationship between overvoltage and melting point necessary. This work has, unfortunately, only been in alkaline solutions, whereas the paper by me on overvoltages and melting points referred to acid solutions. In order, however, to try to find some reason for Prof. Partington's results, the conclusions arrived at in alkaline solutions have been applied to acid solutions. Whether this is justifiable or not cannot be decided until further work has been conducted on the subject. It will be remembered that when Sand and Weeks measured the overvoltage of antimony in alkaline solutions and its variation with hydroxyl ion concentration, they put forward the idea that other metals might have an identical overvoltage. This seems to be the case in some of the cases which have been examined.

This fact, however, by no means nullifies the author's conclusion described in *The Chemical News*, that the metals may be divided into the two groups: one with metals of high overvoltage and low melting point, and one with metals of low overvoltage and high melting point. Although this was the main conclusion arrived at in my previous paper, Prof. Partington has nothing to say on the subject. I should like to put forward here, therefore, the hypothesis that perhaps most of the metals in Group I. of low melting point will be found to have the same high overvoltage. When the results of Sand and Weeks on the overvoltage of all the metals in Group I. have been finally arranged, I hope to submit a further communication in which we may finally decide the exact relationship between the overvoltage of a metal and its melting point. Until this time, it seems to me that we may assume as a general working hypothesis the general relationship previously described by me and partially confirmed by Prof. Partington, that high overvoltage points to low melting point, and low overvoltage to high melting point.—
Yours, &c., E. J. WEEKS.

62, *Forest Hill Road, S.E.22,*
August 9, 1924.

NOTICES OF BOOKS.

The Scientific and other Papers of Rai Bahadur Chunilal Basu, M.B., C.I.E., I.S.O., F.C.S., Rasayanchariya, Vol. I., Edited by J. P. BOSE, M.B., F.C.S. Pp. XXIV. + 524. Calcutta, 1924. Price, Rs. 5/-.

In this volume, the scientific and medical papers of the late Dr. Chunilal Basu, well-known to Indian scientists, have been collected. The memoirs have been grouped according to subject under various heads, viz., chemical and pharmaceutical, medical, medico-legal and industrial chemistry. In the chemical and pharmacological section there are interesting articles on analysis of tinned meat, on the alkaloid of the roots of *Rauwolfia Serpentina*, False Bikha a sterol of the roots of *Higrophila Spinosa*, the analysis of plantains, the chemistry and toxicology of *Nerium Odorum*, etc. The medical section includes articles on cases of snake-bite and diabetes, and the prevention of small-pox. The medico-legal section contains records of the important poisoning cases, and an article on Paka oil as an adulterant of mustard oil.

It is interesting to note that the first paper by the late Dr. Bose appeared originally in *The Chemical News* in 1890, and was entitled "The Analysis of certain samples of Tinned Meat." A perusal of the paper after an interval of over thirty years gives the impression that the analysis might have been carried out last year. It was evidently conducted with great care and precision.

The editor is to be congratulated upon his work of collecting and publishing these valuable original papers.

The Simple Carbohydrates and the Glucosides, by E. FRANKLAND ARMSTRONG, D.Sc., PH.D., &c. Pp. VIII. + 193. Fourth Edition. London: Longman's Green & Co., 39, Paternoster Row, E.C.4. 1924. 16s. net.

The isolation of sugar from the sugar-cane has been carried on from early times. The beet sugar industry is also now over a hundred years old. The industry owes much to chemical research, particularly in regard to the latest technical improvements.

Following upon the early work of Kiliani on the constitution of dextrose and lævulose and the cyanhydrin compounds, the monumental researches of Emil Fischer from 1884 onwards, will ever serve as a model of scientific achievement. His skill in the isolation and identification of the many derivatives of various carbohydrates was unique.

Fischer's death in 1919 synchronised with the publication of the previous edition of this monograph. Since then, much has been done towards the complete elucidation of the many problems of sugar chemistry. Prof. Irvine and his co-workers have shown the existence of a third form of the hexose molecule other than the iso-dynamic stereoisomeric α- and β-forms. The new form, γ-glucose, is relatively unstable and easily undergoes oxidation. His recent work on the methyl derivatives of carbohydrates has led to a great increase in our knowledge of their structure.

In America, Hudson and his co-workers have also obtained results of importance. Recently the mechanism of the photosynthesis of carbohydrates and glucosides has received attention, and theories, based on practical results, have been advanced to explain the origin of many complex organic compounds found in plant tissues.

The role played by the numerous hydrolytic and synthetic enzymes is also discussed in this important compilation.

The present edition of the monograph contains over fifty pages more than its predecessor. The bibliography at the end gives a very complete list of the original contributions on this subject.

That Dr. Armstrong's volume in this series of *Monographs on Biochemistry* has reached its fourth edition indicates, in some measure, its scientific and industrial importance. It will remain the standard work until displaced by another edition.

Applied Chemistry, by Ira D. Garard, Ph.D. Pp. VI. + 496. London and New York: The Macmillan Company. 1924. 15s. net.

This volume, which assumes an elementary knowledge of chemistry, deals with the applications of the science to every-day domestic and industrial life. It is intended for general as well as purely scientific readers.

The author has attempted to correlate much practical information, and many of the general principles have been stated and exemplified in early chapters, thus enabling the reader to follow more easily the later developments.

Air and water are studied, after an introduction, in detail, with special reference to the requirements of human life. The subject of foods and nutrition and the chemical processes involved in this connection have been adequately treated. In chapters XV. to the end, which constitute the most characteristic portion of the book, an account is given of some of the applications of chemical science to industrial processes. Toilet articles and cleansing agents; clothing; textiles, rubber leather, paints, inks, metals, glass and fuels are considered from the chemical point of view. It will be seen that these are in general fairly representative of the industries involving considerable application of a knowledge of chemical science. The author has, of necessity, had to select from many possible subjects. A number of other important applications of chemistry could have been included, and the references to others (*e.g.*, photography, which is very briefly dismissed) might well have been extended.

The volume makes a welcome addition to the more general texts on applied science.

Chemische Reactionen in Gallerten, von Dr. R. E. Liesegang, Zweite umgearbeitete Auflage. Pp. 90. Leipzig and Dresden: Verlagsbuchhandlung Theodor Steinkopff. 1924. Price 85 cents.

If a glass plate is coated with a 5 per cent. gelatin gel containing a little potassium dichromate and a drop of aqueous silver nitrate solution is placed in the centre, a series of concentric rings of silver dichromate will form, alternating with clear zones. Similarly, if an agar-agar gel containing potassium iodide be allowed to set in a test-tube, and a solution of lead nitrate be poured on the surface, a stratum of lead iodide forms at the surface of contact. No lead iodide is formed for a short distance below this, then another stratum of the precipitate occurs, and so on alternately.

This phenomena of the reactions which occur in colloid gels was first discovered by Dr. Liesegang at the end of last century, and the volume now under review is the second edition of his book dealing with this fascinating subject.

An account is given of the methods of procedure; reactions within and without the gel; the degree of dispersion of the reaction products; hydrolytic splitting; rhythmic precipitation; the separation and solution of calcium compounds in gels, etc.

It may not be generally known that a paper entitled *A Study in Rhythmic Series of Chemical Changes*, by K. C. Viraraghava appeared in *The Chemical News*, 1923,

CXXVII., 289 (May 11), in which the author surveyed this comparatively unexplored field of research. The importance of a study of these phenomena is not confined to the research laboratory. Tanning processes are of a very similar nature, and the same applies to the treatments given to exposed photographic plates, films and papers to yield finished pictures.

It may also be suggested that geology would benefit by a deeper knowledge of these phenomena.

That Dr. Liesegang himself has utilised his results in this field may be inferred from his numerous studies in the chemistry of photography. J.G.F.D.

Laboratory Experiments in Chemistry, by N. HENRY BLACK. Pp. IX. + 165. London: MacMillan & Co., Ltd., St. Martin's Street, W.C.2. 1923. 5s. net.

This little volume is intended as a guide for demonstrators and others, and is to be used with Black and Conant's "Practical Chemistry."

The experiments selected only involve simple pieces of apparatus and inexpensive chemicals, yet the ground covered by the book is very wide and the way is paved for more advanced work in the various branches of applied chemistry. The book therefore commends itself more particularly to those teachers of chemistry in technical institutes.

Experiments designed to illustrate fundamental facts have been marked with an asterisk.

PUBLICATIONS RECEIVED.

The Department of the Interior, United States Geological Survey, has issued the following bulletins:—

Copper in 1922, by H. A. C. JENISON. Pp. IV. + 304.

Gold, Silver, Copper, Lead and Zinc in Utah in 1922, by C. C. HEIKES. Pp. 377 to 401.

Gold, Silver, Copper, Lead and Zinc in Montana in 1922, by C. N. GERRY. Pp. 453 to 488.

Gold, Silver, Copper, Lead and Zinc in Arizona in 1922, by V. C. HEIKES. Pp. 489 to 518.

Gold, Silver, Copper, Lead and Zinc in Colorado in 1922, by CHARLES W. HENDERSON. Pp. 519 to 556.

Cobalt, Molybdenum, Nickel, Tan, Talcum, Titanium, Tungsten, Radium, Uranium and Vanadium in 1922, by FRANK L. HESS. Pp. 557 to 583.

Gold, Silver, Copper, Lead and Zinc in California and Oregon in 1922, by JAMES M. HILL. Pp. 405 to 451.

Feldspar in 1922, by FRANK J. KATZ. Pp. 251 to 259.

Stone in 1922, by G. F. LOUGHLIN and A. T. COONS. Pp. 261 to 344.

Carbon Black roduced from Natural Gas in 1922, by G. B. RICHARDSON. Pp. 345 to 346.

Natural-Gas Gasoline in 1922, by G. B. RICHARDSON. Pp. 347 to 351.

Natural Gas in 1922, by G. B. RICHARDSON. Pp. 353 to 358.

Sulphur and Pyrites in 1923, by H. M. MEYER. Pp. 1 to 6.

Gravel Deposits of the Caddo Gap and De Queen Quadrangles, Arkansas, by HUGH D. MISER and A. H. PURDUE. Pp. 15 to 27.

Geology and Ore Deposits of the Manhattan District Nevada, by HENRY G. FERGUSON. Pp. IX. + 163.

Geologic Literature in North America, 1785-1918, by JOHN M. NICKLES. Pp. 1 to 1,167.

Coal Resources of the Raton Coal Field, Colfax County, New Mexico, by WILLIS T. LEE. Pp. VI. + 254.

The Ruby-Kushokwim Region, Alaska, by J. B. MERTIE and G. L. HARRINGTON. Pp. VI. + 129.

Geology of the Coastal Plain of Texas west of Brazos River, by ALEXANDER DEUSEN. Pp. XII. + 137.

The Evolution and Disintegration of Matter, by FRANK WIGGLESWORTH CLARKE. Pp. 51 to 86.

An Early Eocene Florule from Central Texas, by EDWARD WILBER BERRY. Pp. 87 to 92.

DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS.

Development of a Method for Measurement of Internal Stress in Brass Tubing, by ROBERT J. ANDERSON and EVERETT G. FAHLMAN. Pp. 229 to 241.

Some New Thermoelectrical and Actinolectrical Properties of Molybdenite, by W. W. COBLENTZ. Pp. 375 to 418.

New Patents.

THIS list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

Latest Patent Applications.

17645—Busch, A.—Manufacture of acid calcium lactate. July 23.

17722—Meyerhofer, A. F.—Production of hydrofluosilic acid. July 24.

17742—Zeche M. Stinnes.—Purification of crude ammoniacal liquors. July 25.

Specifications Published this Week.

218694—Cowburn, A. W.—Process of and means for the production of concentrated sulphuric acid.

Abstract Published this Week.

216695—Lead and zinc chlorides; sulphur; alloys; electrolysis.—Ashcroft, E. A., 32a, Liverpool Street, London.

Ores, concentrates, &c., containing zinc are chlorinated by chlorine or sulphur chloride at 600-700° C. in known manner, preferably with the addition of carbon if much oxygen is present, any arsenic, antimony or tin present being expelled as chlorides, which may be condensed. The iron and some or all of the lead and silver are precipitated from the melt by adding the requisite quantity of zinc, forming a non-fused granular alloy which, after washing, is smelted for the metals. The sulphur and some zinc chloride liberated in the chlorination are received in a condenser, the sulphur condensing as a layer upon the surface of a strong solution of zinc chloride in the condenser, while the zinc chloride vapour condenses and dissolves in the solution. From time to time zinc chloride solution is withdrawn from the condenser, mixed with fresh ore, and the mixture dried and fed to the chlorinating apparatus, and the solution in the condenser is made up with the wash water of the iron-lead alloy. The purified zinc chloride or zinc and lead chloride is electrolysed, and the chlorine is employed again for treating fresh ore. The electrolysis is preferably effected in the apparatus described in Specifications 198024 and 208649, and the products successively deposited are, when nearly all the lead has been deposited, first impure zinc containing lead, copper, &c., and then pure zinc, or, when the melt contains a substantial quantity of lead chloride first an alloy of lead, silver, &c., then pure lead, then a lead-zinc alloy, and finally pure zinc. The presence of some manganese during the electrolysis is advantageous, and a manganese compound may be added if manganese is not present in sufficient quantity. In a modification the chlorination is effected at a low temperature with sulphur chloride, as described in Specification 200,701, and the product (containing sulphur and sulphur chloride) is introduced into fused zinc chloride at 400-450° C., the mixture being treated with zinc to precipitate the iron-lead alloy and the purified melt being then electrolysed, when chlorine and sulphur chloride are evolved; or the mixture of the chlorinated ore and zinc chloride may be heated to 600-700° C., for instance, by feeding it into a previously obtained melt kept at that temperature, when sulphur is distilled off, leaving a chloride melt which is treated with zinc and subsequently electrolysed as before.

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THE CHEMICAL NEWS,

VOL. CXXIX. No. 3359.

THE RELATIONSHIP BETWEEN ATOMIC NUMBERS OF ALLIED ELEMENTS.

By J. C. Thompson

Relationships between atomic weights have been studied for about a century. A few isolated instances of relationships between similar elements have been determined, but no complete scheme has yet been put forward. So much time has been spent on this subject, that many have come to the conclusion that no relationship exists. Should such relationships be determined they would probably throw important light on the manner in which atoms are built up. In recent years there have been two important discoveries which have almost solved the problem of the construction of atoms

(1) The discovery of atomic numbers;
(2) The discovery of isotopes.

The realisation of the importance of atomic numbers and their complete determination was largely due to X-ray work of Moseley shortly before the war.

The great fact that appeared with complete determination of atomic numbers was the properties of atoms depended on their atomic numbers, and had little to do with their atomic weight. The discovery of isotopes seems to have settled this point.

The arrangement of the elements in a form which showed their inter-relationships started in 1864 with Newlands' Octave Law, and passing through Mendeleléeff's table, which has now reached its best form in the Wedge Periodic Table (see Loring, "Chemical News," December 29th, 1922).

The scheme given here might be considered as an arithmetical interpretation of the Wedge Table. There are, however, several important points which appear from this arithmetical treatment. For instance, the relationship between Hafnium and Zirconium, and the existence of two totally different elements with the same atomic number, 68, that is Erbium, and the Inert Gas of Sir J. J. Thomson atomic weight 167.

The Rydberg series equation for atomic numbers of inert gases reads thus:—

He $2 = 2(1^2)$
Ne $10 = 2(1^2 + 2^2)$
A $18 = 2(1^2 + 2^2 + 2^2)$
Kr $36 = 2(1^2 + 2^2 + 2^2 + 3^2)$

That is stopping off at each squared term the atomic numbers of inert gases is obtained.

It follows from this if one be added to each term a similar series equation is given for Li, Na, Rb, Cs, etc., thus:—

Li $3 = 2(1^2) + 1$
Na $11 = 2(1^2 + 2^2) + 1$
K $19 = 2(1^2 + 2^2 + 2^2) + 1$
Rb $37 = 2(1^2 + 2^2 + 2^2 + 3^2) + 1$
etc.

Similarly, the halogen series might be obtained by using −1. Other groups, too, can be built up similarly.

This series equation is not, however, perfect, since:—

1.—It is not strictly symmetrical.

If it were symmetrical the second term would be for inert gases $2(1^2 + 1^2)$.

2.—There are groups of elements known to be allied which will not give a Rydberg equation, thus: Li 3, Na 11, Cu 29, Ag 67, Au 79.

Both of these difficulties are overcome by the following series equation.

Atomic Number.

He $2 = 2 \times 1$
Ne $10 = 4 \times 1 + 2 \times 3$
A $18 = 6 \times 1 + 4 \times 3$
Kr $36 = 8 \times 1 + 6 \times 3 + 2 \times 5$
Xe $54 = 10 \times 1 + 8 \times 3 + 4 \times 5$
Niton $86 = 12 \times 1 + 10 \times 3 + 6 \times 5 + 2 \times 7$

or

1×2
$2 \times 2 + 1 \times 6$
$3 \times 2 + 2 \times 6$
$4 \times 2 + 3 \times 6 + 1 \times 10$
$5 \times 2 + 4 \times 6 + 2 \times 10$
$6 \times 2 + 5 \times 6 + 3 \times 10 + 1 \times 14$

In this series every second number has an additional term. The terms are multiples of 1, 3, 5, 7 successively. The multiples increase by two for each successive atomic number.

The atomic numbers of group Li, Na, K, Rb, Cs, will be given by adding 1 to the atomic number of the corresponding inert gas.

All, groups including those which fail with Rydberg, can be solved by this formula by adding on the final term of series one turn sooner or later thus:—

H 1 = 0 × 1 + 1
Li 3 = 2 × 1 + 1
Na 11 = 4 × 1 + 2 × 3 + 1
Cu 29 = 6 × 1 + 4 × 3 + 2 × 5 + 1
Ag 47 = 8 × 1 + 6 × 3 + 4 × 5 + 1
Au 79 = 10 × 1 + 8 × 3 + 6 × 5 + 2 × 7 + 1
K = 6 × 1 + 4 × 3 + 1
Rb = 8 × 1 + 6 × 3 + 2 × 5 + 1

* Note the final term 2 × 5 is picked up by Cu, but not by K. Hydrogen falls into position for both this series and halogen series, thus—

H 1 = 2 × 1 − 1
F 9 = 4 × 1 + 2 × 3 − 1
Cl 17 = 6 × 1 + 4 × 3 − 1
Br 35 = 8 × 1 + 6 × 3 + 2 × 5 − 1
I 53 = 10 × 1 + 8 × 3 + 4 × 5 − 1
Mn = 8 × 1 + 6 × 3 − 1

Note.—Mn fails to pick up 2 × 5 term.

It will be noticed that the halogen series contains a negative term −1. This is not altogether satisfactory. It also involves a different method of writing the first term, hydrogen, from that used in Li, Na, etc., series.

In H, Li, Na, etc., series, the first number is 0 × 1 + 1, second member 2 × 1 + 1, third 4 × 1 + 2 × 3 + 1. That is, a new term is picked up at each second successive member. Suppose, now, that a new term had been picked up at once by the second member, then—

H 1 = 0 × 1 + 1
F 9 = 2 × 1 + 2 × 3 + 1
Cl 17 = 4 × 1 + 4 × 3 + 1
etc.

H 1 = 0 × 1 + 1
Li 3 = 2 × 1 + 1
Na 11 = 4 × 1 + 2 × 3 + 1
etc.

This shows how both halogen and alkali series develop from hydrogen. It is interesting that the 14 elements, H, Li, Na, K, Rb, Cs, Cu, Ag, Au, F, Cl, Br, I, and Mn all built up with hydrogen as first member have atomic numbers odd, while 6 inert gases all have atomic number even.

The final 1 could be added to first term, giving series:—

H 1 = 1 × 1	H 1 = 1 × 1
F 9 = 3 × 1 + 2 × 3	Li 3 = 3 × 1
Cl 17 = 5 × 1 + 4 × 3	Na 11 = 5 × 1 + 2 × 3
etc.	etc.

An interesting relationship is that of hafnium (Hf) 72, thus:—

Ti 22 = 6 × 1 + 4 × 3 + 4
Zr 40 = 8 × 1 + 6 × 3 + 2 × 5 + 4
Hf 72 = 10 × 1 + 8 × 3 + 4 × 5 + 2 7 + 4

Hf picking up 2 × 7 term at once, instead of missing a member as in Ce 58 = 10 × 1 + 8 × 3 + 4 × 5 + 4.

The inert gas of Sir J. J. Thomson, atomic weight 167. Erbium has atomic number 68 and atomic weight 167.7. Assuming atomic number 68 as in erbium—

Kr 36 = 8 × 1 + 6 × 3 + 2 × 5.

Inert gas 68 = 10 × 1 + 8 × 3 + 4 × 5 + 2 × 7.

picking up 2 × 7 term at once, instead of missing, as in Xe.

It is interesting to see if any other properties of the elements can be determined in a similar manner to the determination of atomic numbers. In the case of atomic weight, this can be done in some of the main groups of elements. The atomic weights compared in the following scheme are the atomic weights of one of the isotopes:—

The Halogens.	Isotopes.
F 3 × 3 + 2 × 5 = 19	19
Cl 5 × 3 + 4 × 5 = 35	35, 37
Br 7 × 3 + 6 × 5 + 2 × 15 = 81	79, 81
I 9 × 3 + 8 × 5 + 4 × 15 = 127	127
The Inert Gases,	
He 1 + 1 × 3 = 4	4
Ne 1 + 3 × 3 + 2 × 5 = 20	20, 22
A 1 + 5 × 3 + 4 × 5 = 36	40, 36
Kr 1 + 7 × 3 + 6 × 5 + 2 × 15 = 82	84, 86, 82, 83, 80, 78
Xe 1 + 9 × 3 + 8 × 5 + 4 × 15 = 128	129, 132, 131, 134, 136, 128, 130
The Alkali Metals.	
H 1 = 1	1
Li 1 + 2 × 3 = 7	6, 7
Na 1 + 4 × 3 + 2 × 5 = 23	23
K 1 + 6 × 3 + 4 × 5 = 39	39, 41
Rb 1 + 8 × 3 + 6 × 5 + 2 × 15 = 85	85·87
Cs 1 + 10 × 3 + 8 × 5 + 4 × 15 = 131	133

Let these three tables now be drawn up with 3 of first term (not counting the first 1 where present) = a, 5 of second term = b, 15 of third term = c.

Halogen Series.	Inert Gases.	Alkali.
		H = 1
F 3a + 2b	He 1 + a	Li = 1 + 2a
Cl 5a + 4b	Ne 1 + 3a + 2b	Na = 1 + 4a + 2b
Br 7a + 6b + 2c	A = 1 + 5a + 4b	K = 1 + 6a + 4b
I 9a + 8b + 4c	Kr 1 + 7a + 6b + 2c	Rb = 1 + 8a + 6b + 2c
	Xe 1 + 9a + 8b + 4c	Cs = 1 + 10a + 8b + 4c
	Rn 1 + 11a + 10b + 6c + 2d.	

When a, b, and c have values 3, 5, and 15 respectively, then atomic weight of one of isotopes is obtained.

When a, b, and c have values 1, 3, and 5 respectively, the atomic *number* of element is obtained.

Example.—Kr.:
Formula 1 + 7a + 6b + 2c.
Atomic Weight $1 + 7 \times 3 + 6 \times 5 + 2 \times 15 = 82$.
Atomic Number $1 + 7 \times 1 + 6 \times 3 + 2 \times 5 = 36$.
Should hydrogen be added to halogen series, then there should be an isotope of hydrogen of atomic weight 3.

THE BROMINATION OF SUBSTANCES CONTAINING A THIAZOLE RING.

PART II.—THE STRUCTURE OF THE BROMO ADDITION PRODUCTS OF THE SUBSTITUTED BENZOTHIAZOLES OF THE TYPE OF DEHYDROTHIOTOLUIDINE AND THE BROMINATION OF DERIVATIVES OF DEHYDROTHIOTOLUIDINE IN ALCOHOLIC AND OTHER SOLUTIONS, AND THE ACTION OF NITROUS ACID ON BROM BENZOTHIAZOLES.

By R. F. HUNTER, B.Sc., A.R.C.Sc., M.S.CHIM., F.C.S.

The formation of addition products with bromine appears to be a characteristic property of the benzothiazoles. The formation of such addition products was first recognised during the researches of Gatterman (*Berichte*, 1889, XXII., 422) on dehydrothiotoluidine, and the investigations of Anschultz and Schultz (*Berichte*, 1889, XXII., 580) on the dehydrothioxylidines. At a later date Hugershoff isolated the brom addition product of 1 amino benzothiazole (*Berichte*, 1901, XXXIV., 3130) by the action of bromine on a chloroform solution of phenyl thiocarbamide, although he did not recognise it as such till two years later.

It has been suggested by the author (*The Chemical News*, 1923, CXXVII., 385) that the dibrom addition product of dehydrothiotoluidine has the structure (1) and is formed by the normal fission of the double bond between the nitrogen and carbon atoms of the fused heterocyclic ring with the addition of bromine at the positions (1) and (2). If this suggested mechanism is correct, it is clear that the reaction by which dehydrothiotoluidine dibromide is formed should be a general one and be given by all compounds of this type which contain the fused thiazole ring.

$$CH_3C_6H_3 \overset{S}{\underset{NBr}{<\quad>}} CBr\ C_6H_4NH_2$$

(1)

$$CH_3C_6H_3 \overset{S}{\underset{NBr}{<\quad>}} CBr\ C_6H_4NHCOMe$$

(2)

With the view as to the establishing of the suggested hypothesis, the bromination of a number of derivatives of dehydrothiotoluidine has been examined, a number of brom addition products have been isolated, and it appears that the reaction first observed by Gatterman is a general one. Owing to the fact that the quantity of brom addition products, particularly with regard to the more complex thiazoles, used

was small, it was not possible to make an exhaustive study of the compounds isolated. It is desired at this point, however, to place a somewhat puzzling observation on record, and that is, that nitrous acid or an acidified solution of an alkali nitrite reacts with brom benzothiazoles of the type of dehydrothiotoluidine, dibromide liberating free bromine. It is unfortunate that this reaction involves the production of much tar and that it has up till the present not been possible to isolate definite products. Light was, however, thrown on this fact by an examination of the action of sulphurous acid on dehydrothiotoluidine dibromide, sulphurous acid reduces dehydrothiotoluidine dibromide with the production of hydrobromic acid and sulphuric acid, the sulphurous acid acting as a reducing agent. It will be recalled that nitrous acid frequently acts similarly as a reducing agent, and this explains the peculiar action of nitrous acid in liberating bromine. For it would appear that a portion of the nitrous acid reduces the brom benzothiazole, in the same manner as sulphurous acid reduces the brom benzothiazole, the nitrous acid being oxidised to nitric acid, this and hydrobrom c acid can react to form nitric oxides with the liberation of free bromine, or possibly only part of the bromine is converted into hydrobromic acid, the rest being liberated as free bromine. The liberation of bromine from a brom benzothiazole by the action of nitrous acid appears, then, to be due to the reducing properties of the latter reagent. The tarring which is observed is quite readily understood when we remember that the free amino group in dehydrothiotoluidine dibromide is converted into a diazonium nitrate grouping by the nitrous acid, and at room temperature this will commence to be converted into a hydroxyl group with the splitting off of nitrogen in the usual manner.

With regards acetyl dehydrothiotoluidine dibromide, the instability of this compound is somewhat peculiar in view of the stability of dehydrothiotoluidine dibromide and also of the brom addition product of 4′ benzalamino 1 phenyl 5 methylbenzothiazole. It would appear that the acetylation of the amino group, strange though it appears, is responsible for the remarkable decrease in stability of the brom benzothiazole, on passing from dehydrothiotoluidine to *acetyldehydrothiotoluidine*.

It will be recalled that during the investigation on the reactions of the amino group in dehydrothiotoluidine, that a compound was isolated which was obtained by the action of sulphur monochloride on a xylene solution of the thiazole, for which the structure (3) was suggested. If the compound had this structure, it should clearly add four bromine atoms to give the tetrabromthiazole (4), actually the compound (3) does form a brom addition product of the usual type when brominated in alcoholic solution.

$$[CH_3C_6H_3SNCC_6H_4NH]_2S:S$$
(3)

$$[CH_3C_6H_3 <^{S}_{NBr}> CBr\ C_6H_4NH]_2S:S$$
(4)

Similarly the thio urea of dehydrothiotoluidine should add four bromine atoms in alcoholic solution to give the tetrabrom thiazole (5), and in the same way the compound formed by the condensation of dehydrothiotoluidine with acetaldehyde in alcoholic solution as previously described (*loc. cit.*) should add our bromine atoms to give the tetrabromo benzothiazole (6).

$$[CH_3C_6H_3 <^{S}_{NBr}> CBr\ C_6H_4NH]_2:C:S$$
(5)

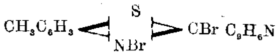
$$^{CH_3}_{H}> C:[NH\ C_6H_4\,CBr <^{S}_{NBr}> C_6H_3CH_3]_2$$
(6)

In a precisely similar manner, the quinoline of dehydrothiotoluidine which is formed by heating the thiazole with arsenic acid, glycerol and sulphuric acid at a temperature in the neighbourhood of 200° C., should brominate in alcoholic solution to give a dibromo addition product (7) by the normal fission of the double bond of the fused heterocyclic ring and the addition of bromine at the nitrogen and carbon atoms as in the case of the parent substance: dehydrothiotoluidine.

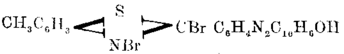
With regard to the bromo quinoline derivative, it will be recalled that although dehydrothiotoluidine is odourless, the quino-

line of the compound formed by Skraup's reaction is a compound having a tobacco-like odour, this effect being attributed to the introduction of a second tertiary nitrogen atom into the molecule of the benzothiazole, it is worthy of note that this odour is lost on the addition of bromine.

1 Phenyl 5 methyl benzothiazole 4′ azo β naphthol, the azo dye prepared by coupling a diazotised solution of dehydrothiotoluidine with β naphthol, it will be recalled, is soluble in glacial acetic acid, in fact glacial acetic acid was the solvent employed for crystallisation to obtain a pure specimen (*loc. cit.*). A glacial acetic acid solution of the compound was therefore brominated in the usual way, when the usual type of brom thiazole was thrown down, which is assumed to have the structure (8).



(7)

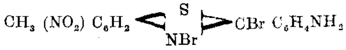


(8)

With regard to 1 phenyl 5 methylbenzothiazole 4′ azo β naphthol, it will be observed that the molecule is unsaturated in two places, firstly between the nitrogen and carbon atoms of the fused thiazole ring, which are joined by a double linkage, and secondly at the azo linkage, where two nitrogen atoms are joined by a double bond.

And it might, on this account, be suggested that as the double nitrogen carbon linkage in the thiazole ring is ruptured with the addition of two bromine atoms in compounds of the type of dehydrothiotoluidine and acetyldehydrothiotoluidine, that there might exist the possibility of brom addition at the azo linkage in 1 phenyl 5 methylbenzothiazole 4′ azo β naphthol, that is to say, that there might exist a possibility of bromine addition at both unsaturated parts of the molecule of the compound, although if this were possible, there can be little doubt that the compound so obtained would be explosively unstable, for bromine directly linked to a nitrogen atom is an unstable configuration, while the brom addition product obtained by brominating a glacial acetic acid solution of the thiazole dyestuff is quite stable. The point, however, was noteworthy, and a glacial acetic acid solution of a similarly constituted compound: the dye formed by coupling diazotised sulphanilic acid and beta naphthol was therefore brominated under the same conditions as employed in the case of the thiazole dyestuff. No precipitation of a brom addition product took place, and the dye was precipitated to all intents and purposes unchanged by adding water to the solution, after standing for an hour, in contact with an acetic acid solution of bromine.

It will be recalled that nitro dehydrothiotoluidine formed by the direct nitration of dehydrothiotoluidine with the fuming acid at ordinary temperatures, dissolves in glacial acetic acid. Nitro dehydrothiotoluidine which contains the unchanged fused thiazole ring should clearly be capable of bromination to yield the brom thiazole (9).



(9)

Actually on brominating a glacial acetic acid solution of nitro dehydrothiotoluidine, a brom addition product is thrown down as a brown but tarry precipitate, with which little can be done, but the observation is nevertheless of interest. A similar difficulty was experienced when a glacial acetic acid solution of 5 nitro 1 phenyl benzothiazole was brominated. A bromo compound was precipitated, but in a sticky, tarry state with which nothing could be effected. With regard to this tendency to tar during bromination in solutions of benzothiazoles, the matter appears to be connected with the speed at which the bromine is run in. For this reason the use of the burette is recommended, in which case the bromine can be regulated easily. The bromine should always be added slowly to the solution with stirring. Rapid addition frequently causes tarring in otherwise simple precipitations.

EXPERIMENTAL.

Dehydrothiotoluidine dibromide:

5 gms. of dehydrothiotoluidine are dissolved in 100 ccs. of alcohol in a 350 cc. beaker. The solution is cooled to room temperature, while 2 ccs. of bromine are added drop by drop from a burette with

stirring. The precipitated bromo thiazole is allowed to stand for twenty minutes and then filtered, washed with a little alcohol and cold distilled water till free from bromine, and finally again with a little alcohol, and allowed to dry in a desiccator. The substance so prepared is a fine dark brown powder, which is quite stable to boiling water. Analysis:—

0.2100 gm. of brom thiazole gave 0.1850 gm. AgBr.

Per cent. Br calculated = 40 per cent.
Per cent. Br found = 38.1 per cent.

Acetyldehydrothiotoluidine dibromide:

2 gms. of acetyl dehydrothiotoluidine are dissolved in 40 ccs. of glacial acetic acid To the solution is then added 1 cc. of bromine from a burette, drop by drop with stirring. A yellow precipitate settles out, which is filtered, washed with much cold water and a little alcohol, and dried in a desiccator. The compound is very unstable and loses bromine on keeping. The specimen analysed in this investigation had unfortunately been kept for some time before the estimation and gave poor figures for halogen. This, however, is not remarkable, since even at ordinary temperatures, in a dry state, the brom thiazole smells strongly of bromine. Analysis:—

0.2000 gm. of brom acetyl compound gave 0.112 gm. of AgBr, after having been kept for a week.

Bromination of compound obtained by condensation with sulphur chloride:

1 gm. of the condensation product obtained from sulphur chloride and dehydrothiotoluidine (*loc. cit.*) is dissolved in warm alcohol and the solution cooled in a 350 cc. beaker. Bromine is then added drop by drop from a burette with stirring, as in the previous cases. The brown brom thiazole collected, washed with a little alcohol and dried.

Bromination of di-dehydrothiotoluidine thio urea:

1 gm. of the thio urea is dissolved in the minimum of warm alcohol, the solution cooled to room temperature in a beaker, and bromine added drop by drop with steady stirring, when a very dark brown brom thiazole separates. This is filtered after standing for ten minutes or more, washed with alcohol, distilled water, and then again with alcohol, and dried.

Bromination of condensation product of dehydrothiotoluidine and acetaldehyde:

1 gm. of the condensation product obtained by condensing an alcoholic solution of dehydrothiotoluidine with the necessary acetaldehyde is dissolved in alcohol in a beaker as before, the solution cooled to room temperature, and bromine added drop by drop from a burette, as in the previous cases. The brown precipitate is allowed to stand for a few minutes, and washed with alcohol and water.

Brom quinoline of dehydrothiotoluidine:

A small amount of tbe quinoline, prepared by condensing dehydrothiotoluidine with glycerol, arsenic acid and sulphuric acid at 200°, is dissolved in alcohol to give a fluorescent solution. The solution of the quinoline is cooled to room temperature, and bromine added drop by drop with stirring, when the usual type of brom benzothiazole separates. The solution and precipitate is allowed to stand for a few minutes and filtered. The brom benzothiazole was washed on the filter paper with alcohol, water, and then alcohol, as before. A further amount of the substance can be obtained by adding water to the alcoholic filtrate, but this is generally much more impure and by no means as clean a product as the brom thiazole precipitated during the addition of bromine.

1 Phenyl 5 methylbenzothiazole 4′ azo β naphthol bromide:

About 0.3 gm. of the dye obtained by coupling diazotised dehydrothiotoluidine with alkaline beta naphthol is dissolved in glacial acetic acid in a beaker, the bright red solution filtered from any insoluble matter or excess thiazole, cooled down to room temperature in a 250 cc. conical flask. Bromine is added drop by drop from a burette with gentle shaking of the flask. A brown red precipitation of the addition product takes place at once. Bromine is added till excess is present, and the liquid in the flask smells strongly of the halogen. The flask is allowed to stand for ten minutes, the precipitate filtered off, and the bromo compound washed with alcohol, water, and a little alcohol and dried.

Bromination of Orange II.:

A small quantity of Orange II., obtained by coupling diazotised aniline parasulphonic acid with alkaline β naphthol, is dis-

solved in glacial acetic acid. The solution is cooled and bromine added drop by drop from a burette. No precipitation occurred. The liquid in the beaker was therefore left to stand for two hours. At the end of this time, nothing having been deposited, water was added, when the orange dye was re-precipitated, apparently quite unchanged.

Nitrodehydrothiotoluidine bromide:

0.5 gm. of nitrodehydrothiotoluidine prepared by dissolving dehydrothiotoluidine in fuming nitric acid at room temperature, precipitating the product with water, and converting into the free base by means of ammonia, is dissolved in warm glacial acetic acid, the solution cooled in a beaker, and bromine added slowly drop by drop from a burette. A tarry bromo compound separates. The tarring is much reduced by adding the bromine gradually and avoiding the presence of much excess of the halogen in the solution.

The Chemical Laboratory,
St. Mary's Road, N.1,
August, 1923; and

The Chemical Laboratory,
Highbury New Park, N.5,
May, 1924.

THE SILICATE OF SODA PROCESS FOR CONCRETE.

The advantages of concrete in general constructional work are now widely recognised, and the buildings at the British Empire Exhibition, Wembley, are a striking example of the remarkable progress that has been made. Incidentally, it may be mentioned, that in the Concrete Utilities Bureau, at the Exhibition, there will be found references to over 90 different uses of concrete.

The value of this material is still further enhanced, because of the perfection of the simple and inexpensive silicate of soda process of hardening, due to the extensive research work which has been devoted to the subject for a number of years past.

Prominent in this field is the well-known firm of Messrs. Brunner Mond & Co., Ltd., who have just issued a new and enlarged edition of their extremely interesting pamphlet, "Silicate of Soda and Concrete," to be had on application to their head office, Northwich, Cheshire, which gives a very clear and concise description of the whole process.

It is well-known, of course, that silicate of soda is manufactured by fusing together a good grade of sand (silica, SiO_2) with soda ash (Na_2SO_3), the glass-like product being usually dissolved in water under special conditions and sold as an almost colourless liquid. This is then further diluted and sprayed over the surface of the concrete, which must be clean and dry, and results in the formation of a dense and hard outer layer. As a consequence, however, of the detailed research work mentioned, it is now known that to enable the best results to be obtained a silicate of soda of the correct grade or "ratio" must be used, with a fairly high proportion of silica to soda. Messrs. Brunner Mond supply for this purpose a grade known as P.84, which has a ratio of 3.3, that is to say, 3.3 molecules of silica (SiO_2) combined with 1.0 molecule of soda (Na_2O_3), and is found by experience and research to give excellent results.

Further, also, the commercial silicate of soda solution must be sufficiently diluted, say, one part with four parts of water, so that it may penetrate freely the surface of the concrete, to a depth of $\frac{1}{4}$-$\frac{1}{2}$-inch. As explained clearly in the above publication, the formation of an intensely hard and dense outer layer is due to the formation within the pores of the concrete of calcium silicates and free silica. The formation of calcium silicates takes place because free calcium hydrate has been separated in the setting of cement by the water used in mixing decomposing poly-calcium silicates, and this reacts with the dilute sodium silicate solution.

It will be remembered that the formation of free lime in the setting of cement was first discovered by Le Chatelier, who expressed the action by the following equation:—

$$3\ CaO.SiO_2 + Aq = CaO.\ SiO_2\ Aq + Ca(OH)_2$$

Special attention is given in the new edition to the value of the silicate of soda process in hardening concrete roads to resist the modern heavy motor traffic, and particularly valuable also in the case of concrete floors is the elimination of dusting. Further, there is also discussed the applica-

tion of silicate of soda to concrete in the case of oil tanks, water tanks, and sea walls, since another beneficial effect is a much increased resistance to permeation by water and by oil. In addition, it should be emphasised that the process is not expensive, costing less than ½d. per square yard for the three coats necessary. The actual hardening effect on concrete is also being shown on Messrs. Brunner Mond's Stand at the Chemical Section, Wembley, by means of a motor-driven abrasion machine, in which blocks of sand cement, one-half of which has been treated with silicate of soda solution, are subjected to the rubbing action of two heavy pieces of steel. The untreated portion is seen to be worn away whilst the other is little affected, a very striking demonstration.

THE BRITISH ASSOCIATION.

[TORONTO MEETING.]

Presidential address to Section B, by SIR ROBERT ROBERTSON, F.R.S., entitled *Chemistry and the State.*

(Continued from last week.)

A new phase was entered with the declaration of war, and ultimately all chemical help was mobilised for the defence of the realm. A nucleus existed at Woolwich, where the small staff of eleven chemists had been occupied in the study of explosives and their application. In two directions this experience proved of importance, for it enabled immediate answers to be given to questions which would otherwise have necessitated protracted storage trials, and it afforded the staff the training necessary to qualify them to meet the fresh demands that became urgent on the outbreak of hostilities.

After the beginning of the war the increase of work imperatively called for a larger staff, and more chemists were appointed, until at the beginning of 1917, the home supply being exhausted, permission was obtained to withdraw from France members of the Special Brigade, R.E., of whom more than thirty were transferred to the Department. Finally, the chemical staff numbered 107 chemists and physicists distributed in an organisation which had been gradually evolved, comprising sections for dealing with different classes of work, such as organic chemistry, physical chemistry, analytical and general chemistry, physical investigation, calorimetry, stability, pyrotechny, applications of high explosives, fuze design, and records.

The manufacture of high explosives had not previously been undertaken by Government, and the known processes for making trinitrotoluene, which was early chosen as a Service high explosive, were unsatisfactory. One of the first subjects, therefore, taken up after the outbreak of war was the provision of efficient and rapid process for the manufacture of trinitrotoluene, especially without the use of fuming sulphuric acid (oleum). From the results of a large series of nitrations in the laboratory, a process was evolved characterised by several novel features, and this was put to the proof on the semi-industrial scale of a quarter ton, a plant being designed and erected in the Research Department, Woolwich, for nitration, including appropriate arrangements for the mixing and concentration of acids. This small plant substantiated in a remarkable way the process evolved from the laboratory work, and from the start turned out trinitrotoluene of good quality and yield. The process found immediate application in the large Government factories that were designed and erected by Mr. Quinan and also in numerous private works built at this time. The small-scale plant mentioned was used also for the purpose of training chemists, who proceeded to operate chemical plant in Government and private factories.

A study of trinitrotoluene in all its aspects was undertaken, and much attention devoted to its chemistry, the proportions in which the isomers occur in the crude product being determined by thermal analysis, and investigations were made on their interactions, stability, sensitiveness, heat values, and explosive properties. Most of the scientific results of this work have since been published.

When it became evident, as it soon did to Lord Moulton, that the supply of high explosives in use, lyddite and trinitrotoluene, would not suffice, the Research Department put forward mixtures of ammonium nitrate and trinitrotoluene, the amatols, as a result of a study of their properties and of their effects in shell-bursting trials. Gun trials confirmed these trials at rest, and the adop

tion of amatol as a high explosive quickly followed. Various methods of filling these mixtures into shell were at this time worked out, and many of them were applied on the very largest scale.

It was found that 80/20 amatol (80 parts of ammonium nitrate to 20 of trinitrotoluene) was less easy to bring to detonation than lyddite or trinitrotoluene itself, and it required special arrangements in the train of initiation of detonation. These were successfully devised, and good and trustworthy detonation of our shell was secured. Ultimately, amatol became practically the only explosive for land and aerial warfare, and justified the early estimate of its properties and capabilities. It is economical in that it makes use of a cheap ingredient, and has explosive properties that render it very suitable for the purposes for which it is used. In 1917 the production was at the rate of about 4,000 tons a week.

The Department continued the study of amatol, especially with regard to its chemical stability and compatibility with the various materials with which it came into contact. Certain impurities in ammonium nitrate were discovered to be objectionable, and investigation of these led to an improvement in the purity of the ammonium nitrate supplied. The manufacture of amatol and the modes of filling it into shell occupied the attention of a large staff of chemists attached to the factories, and an increase in knowledge of its chemical and physical properties led to improved methods of handling it.

The Service propellant cordite required for gelatinisation in the course of its manufacture the solvent acetone, of which the supply ran short when the programme for propellants began to exceed all previous calculations. To meet this situation, cordite of the existing type was retained for Naval Service, but for Land Service a modification was introduced under the name of cordite R.D.B. (Research Department powder 'B'). This propellant could be made without any alteration in the plant required for the manufacture of cordite. Instead of acetone the solvent employed was ether-alcohol, and instead of guncotton a lower nitrate of cellulose was used. The great factory at Gretna, also built by Mr. Quinan, manufactured cordite R.D.B. exclusively, and this soon became the only propellant made in this country for the Land Service. It was produced both by Government and by private firms in enormous quantities. The alcohol was made in the country from grain, and ether was produced from it, so that dependence on sea-borne solvent was reduced. It was this need for alcohol that led to the restrictions imposed on that liquid when used as a beverage.

Numerous problems arose in connection with these manufactures as they developed and in the application of the explosives in the various types of ammunition, and these necessitated the study of the explosives in all their aspects. A large addition to the knowledge already existing was thus acquired on the more theoretical side of the study of explosives, and much of this has been made available by publication.

As the demand on our resources increased, and the necessity grew for investigating every source of supply and possible alternative, it came to pass that nearly every professor of chemistry in the country was mobilised for investigation in this field and in that of chemical warfare, and much valuable work was done by them, both of a research and inspectional nature.

For the manufacture of explosives and the operation of filling them into munitions of various kinds in the existing factories and the new ones which sprang up, a large staff of chemists, amounting to about 1,000, was required, and in this way many chemists whose earlier work lay in quite other directions, such as at the universities or in teaching posts, received an insight into technology and took control of workmen.

During the war itself, instructional work in this subject was not wanting, for current progress in the factories under his control was discussed in a systematic manner by Mr. Quinan with representatives of his staff, a course which led to important improvements. Although most of these wartime plants for the manufacture of explosives have been dismantled, much of the technical experience gained has been saved, and will be found incorporated in a series of memoirs (Technical Records of Explosives Supply) published by H.M. Stationery Office. The information set forth in these volumes is in a form which has a much wider appeal than to the explosives

technologist only, and their study is commended to those who take up the subject of chemical technology in any of its aspects.

In addition, factories for the production of substances not in themselves explosive equally required the services of chemists, and many were employed in the production of such substances as methyl alcohol, acetone, and acetic acid.

Instruction in chemistry is provided by the Fighting Services for Naval and Marine cadets at Dartmouth, and for Army cadets at the Royal Military Academy and the Royal Military College, Camberley. For selected officers, both of these Services have a professional staff for providing systematic courses in theoretical and practical chemistry, with special reference to Service applications, at the Royal Naval College, Greenwich, and at the Artillery (formerly the Ordnance) College, Woolwich.

DEFENCE—CHEMICAL WARFARE.

While our well-developed position of the great inorganic chemical manufactures was a source of strength when the demand came during the war for an enormous production of ammonium nitrate, for example, our neglect to foster a great organic chemical industry led to dangerous delays and improvisations. This was apparent from the beginning when several universities had to co-operate to produce a sufficient supply of local anæsthetics, and when presently our lack of dyes, photographic developers and sensitisers revealed our former dependence on foreign supplies. In November, 1914, the Royal Society had set up a Committee to assist the Government, and this became an Advisory Committee when, after May of the following year, the gas attack caused the British Government, which up till then had scrupulously refrained from its use, to retaliate with that weapon. Special companies were created of chemists whose work often had little of a chemical aspect, but many of these men, in twelve to eighteen months, had to be withdrawn for research and control of plant. Chemical advisers were appointed to the armies and for liaison purposes, a central laboratory for rapid identification was established in France, and co-operation was effected with the physiologists. At home assistance was afforded to chemical contractors, and the manufacture of respirators to meet needs rapidly becoming more complex was carried out with great vigour and efficiency. The increasing importance of gas warfare led to a proving ground at Porton being acquired, when the research which had been carried out at the Imperial College at South Kensington became centralised there. As the final proof of explosive projectiles is carried out at Shoeburyness, it was now possible on this new proving ground to settle questions relating to the filling and correct performance of chemical shell, thus enabling the Chemical Warfare Designs Committee to recommend ammunition to meet the needs of a situation which was continually developing, until the proportion of chemical shell compared with high explosive shell was finally a large one.

In the ramifications of this work all the chemical skill in the universities not already applied to explosives was mobilised, since the demand for new designs involved the manufacture of new substances for shell, bombs, and grenades, new smoke and incendiary compositions, and continuous research and experimental work both on the offensive and defensive sides.

In a few cases only was the country capable of expanding its existing manufactures, as in the case of phosphorus and chlorine; it was not equipped for the home production of phosgene, arsenical compounds, or mustard gas. New factories had, therefore, to be erected and staffs specially trained, in striking contrast to the existence in Germany of standardised plant capable of rapid transference from one purpose to another with little alteration: an example of this was their manufacture of arsenical preparations in the azo-dye sheds.

As a result of an intensive study of absorbent substances, our respirator was never beaten, and it is claimed that, although our output was smaller, the better employment of gas, tactically for surprise, lay with us. Starting late and entering a field entirely new, we were able while there was yet time to protect the soldier, and to make a reply on the offensive side that was rapidly becoming more and more effective.

Not all of the work specially devoted to chemical warfare has been without its effect on peace-time requirements. Thus liquid chlorine, of which very little was made in this country before the war, is now being prepared electrolytically and transported by

rail in tank waggons for use in various industries. For the preparation of phosgene, which had been used in Germany in the manufacture of dyes of the triphenylmethane series, better methods were discovered in this country, so that cheaper and purer phosgene is being used here for the first time to prepare the important group of colours known as the Victoria blues. Improved methods are now available for the manufacture of arsenical compounds, such as arsenic trichloride, a substance used for combating the growth of prickly pear in Australia; and mention may be made of the work of Professor Moureu in France on the stabilisation and concentration of acrolein, as it has led to the production of a substitute for celluloid from that body. In addition, the study of many of the bodies used for chemical warfare has been of value from the aspect of the elucidation of their chemical constitution.

METALLURGY.

When the part played by metals in the history of civilisation is considered, the development of some more durable alloy or some stronger metal appears intimately linked with a distinct advance constituting a new age, often characterised by eponymous association with the metal. As the possession of some superior metal may give ascendency to a people, it is natural that States should show interest in metallurgy, both militarily and to maintain the standard of the medium of exchange. It is thus seen that iron and the precious metals, gold and silver, have for the most part interested the modern State, the metallurgy of the other metals only more recently coming in for attention on military grounds. Accordingly, we find the armourer and the minter holding important positions in early times.

It must be stated at the outset that the relations in Great Britain between the State and metallurgical science before the war of 1914 to 1918 were for the most part sporadic, the great developments in that science being to a large extent independent of the State. It undoubtedly exerted, however, an influence on the nature and quality of metallurgical products, of which it was a large user for warlike, structural, and shipbuilding purposes, by specifying the conditions of their acceptance; standards established by the Government, often based on enquiry and experiment, gave confidence to other users and resulted in the improvement of industrial materials.

Although iron-making had flourished intermittently since the Roman occupation and had reached considerable proportions under Elizabeth, no great contribution to knowledge can be attributed to Great Britain in the progress of metallurgy until the restriction of the cutting down of timber for charcoal towards the end of the sixteenth century forced into consideration the use of coal for smelting, the pioneer work being that of Dud Dudley, who in 1642 cast iron cannon at his foundries for the Royalist troops. It was his experience as an Admiralty official that brought Cort, more than 100 years later, to recognise the inferiority of English wrought iron, and to leave the Service for the purpose of improving existing processes so that his successful wrought iron was accepted towards the end of the eighteenth century for anchors and iron work in the Royal Navy. His invention of the puddling process led to great prosperity in the iron trade.

The need to meet Government requirements became similarly urgent in the case of steel, which in its earlier production as puddled steel so failed in uniformity of composition that as a material of construction it could not be used by the Admiralty, nor permitted by the Board of Trade. Bessemer's great advance of converting molten iron cast into steel by blowing air through it, described in 1856 to this Association, enabled him to propose a material more suitable for guns and projectiles than the cast iron then employed. Bessemer steel came into use for many purposes, and its production increased rapidly, but boiler plates submitted to the Admiralty still showed great variations in carbon content. Meanwhile the rival open-hearth process was steadily developed and established by Siemens. In 1875 the Director of Naval Construction had pointed to the danger due to lack of uniformity of steel made by the converter process, but in 1879 he was able to report the success of the new open-hearth steel. The Government challenge had been taken up by Siemens, who produced a steel to meet all its specifications, so causing its acceptance for Admiralty work, and its admission by the Board of Trade for structural use.

After Thomas and Gilchrist had in 1877 solved the problem of dephosphorising iron by the basic process, the Admiralty instituted an enquiry as to its properties, which led to an official recognition of basic steel, thus greatly enlarging the source of supply through the use of native ores.

Among the men who assisted the Government in these enquiries was Dr. Percy, who placed metallurgy in this country on a scientific basis, while lecturing on that subject at the Royal School of Mines and at the Ordnance College. Abel, appointed War Department Chemist in 1854, gave much attention to the use of iron and steel for military purposes, investigating the question of erosion of guns and throwing new light on the constitution of steel by his isolation of Fe_3C. He did good service in convincing the great ironmasters of the importance of chemistry in their industry. To Roberts-Austen also, Chemist and Assayer to the Mint, many Government enquiries and commissions were indebted for advice on the subjects he had enriched by his researches, such as the physical constants and mechanical properties of metals, the effect of impurities, the cementation of iron, heat treatment, and many others, including the first 'freezing-point' curve of a series of binary alloys in 1875. It was in consequence of these that his co-operation was invited by the Alloys Research Committee, whose first six reports contained a great deal of his work, covered a wide field, and did much towards the realisation by engineers of the value of microscopical and thermal methods in the study of metals. Later reports to this committee, whose work in 1902 was transferred to the National Physical Laboratory, have maintained their high standard, and have been contributed to by such workers as Carpenter, Hadfield, and Rosenhain.

The last of these reports, the eleventh, embodies work at the National Physical Laboratory from 1914 to 1918, the year when that Institution became a part of the Department of Scientific and Industrial Research It deals with light alloys, the need for which the war has emphasised, especially in connection with aircraft. For this purpose the Laboratory's work has resulted in furnishing alloys of aluminium with zinc and copper, with copper and manganese, and with copper, nickel and magnesium, possessing remarkable and useful properties such as high tensile strength at ordinary and also at raised temperatures.

Since the war light aluminium alloys continue to be studied at the National Physical Laboratory, which is the Government establishment where metallurgical research is carried out mainly for the advancement of knowledge. Here has been worked out the constitution of many important systems, binary, ternary, and quarternary, in which aluminium is the largest constituent, and the wire models constructed for the ternary alloys have proved of great value in the study of their constitution. Such questions as age-hardening have been investigated and the cause ascertained.

Systems with copper as the dominant metal have been investigated as regards their constitution, as well as the effect on their mechanical and electrical properties of known additions of other substances that may be present as impurities.

But attention is also being given to ferrous alloys for whose investigation specially pure components have to be prepared, in order to eliminate the effect of impurities of which a very small proportion may often have a marked influence on the product, and several equilibrium diagrams with iron as the main component have been worked out. Research on the more physical side includes investigations on the heat evolved during the plastic deformation of a metal, on the effect of heat treatment and composition on the magnetic properties of tungsten steels, on fatigue, and on the physical constants of metals. By the application of X-ray analysis to the crystal structure of metallic systems, Rosenhain has obtained confirmation of his conception of the nature of solid solutions.

The chemical section of the National Physical Laboratory carries out a large amount of work in connection with these researches, the investigation of methods of analysis, and the preparation of standards for the analysis of steel, as well as chemical work of a non-metallurgical nature.

Maintained by the Fighting Services since 1904 to increase the efficiency of the metals used in the manufacture of ordnance and armament, the Metallurgical Branch of the Research Department, Woolwich, increased in numbers, building and equipment during the war, and at present

employs about 25 metallurgists. It has been occupied for the most part with steel, the heat treatment of which in relation to its mechanical properties has been the subject of close study, resulting in improved gun forgings being delivered by the makers. Two main types of steel have been under consideration, those which would give a minimum yield point of about 35 tons per square inch when treated in large masses, and those at about 25 tons. As a result much information has been acquired on the properties and heat treatment of steel containing various proportions of nickel, chromium, molybdenum and vanadium. The study of the elastic properties and of the erosion of gun steel has been of importance to gunnery. The Moore adaptation of the Brinell hardness test, in which a small ball and load are used in a specially designed machine, was originally developed in the Department for testing small arm cartridge cases, and has since found many other important applications here and elsewhere.

(To be continued.)

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE INSTITUTE OF METALS.

The annual autumn meeting of the Institute of Metals will be held in London on September 8—11. Visitors' tickets admitting to the meeting, also to a lecture—illustrated by kinematograph films—on "Recent Developments in Non-ferrous Metallurgy in the United States," by Mr. W. M. Corse, of Washington, D.C., can be obtained from Mr. G. Shaw Scott, 36-38, Victoria Street, Westminster.

BRITISH EMPIRE EXHIBITION.

THOS. FIRTH & SONS' EXHIBIT.

STAINLESS STEEL.

Firth Stainless Steel is so well known amongst engineers that a great deal of attention is bound to be focussed on this branch of Firth's manufactures. A very wide range of exhibits has been gathered together including the following finished parts:—

A wonderful selection of many different types of turbine blading of 5 per cent. nickel steel are shown, and a particularly interesting exhibit in the form of an actual section removed from a 2,000 K.W. Westinghouse Turbine, steam pressure 200 lbs., superheat 200 F. This section shows 12 blades.

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Stainless Steel is the ideal material for this purpose, giving as it does a brilliant, lasting, and untarnishable surface, without the dual reflection of ordinary plate glass. Stainless Steel gives a perfectly *true* result, and for surgical, dental, optical, and scientific work, may be claimed to be the only satisfactory reflector. A showcase is entirely devoted to this form of application.

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- Stirrups, Spurs and Harness-Room Fittings.
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- Name Plates.
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- Full range of Butchers' Hooks.
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- Complete Fireplace.
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- Railway Carriage Handles.
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- Piston Rod and Cotter.
- A complete Bacon-Slicing Machine, with Stainless Steel Fittings.

NOTICES OF BOOKS.

Einstein's Theory of Relativity, by Prof. Max Born, translated by H. L. Brose, M.A.; pp. xi. + 293. Messrs. Methuen & Co., Ltd., 36, Essex Street, London, W.C.2. 1924: 12s. net.

Relativity literature has a fascination about it unparalleled in the history of science. Every new book is dipped into and studied with keen interest. The reason for this is apparent. There is a deep mystery about relativity, for it involves entirely new conceptions of time and space and yet its entire structure rests upon experiment.

It appears that our basic methods of analysis must involve the doctrine of relativity as applied to time and space with the velocity of light as a constant in the calculations. Events are not simultaneous—as we ordinarily understand simultaneity—if they occur at different places, for each place has a time of its own. This mode of analysis, supported by rigorous equations, gives the correct answers; and in consequence the old idea of the absoluteness as applied to these metrics disappears. If we had lived as an electron in an electron world of far faster movements, we should never have had an absolute Newtonian time system for all relative measurements; but for ordinary movements the change brought about in our measurements by these new ideas does not affect our calculations to a measurable extent.

We have before us the latest work on Relativity by Prof. Born. The publishers (Messrs. Methuen) announce on the outer cover to the volume that Prof. Born's book gives a lucid historical account of Einstein's theory of relativity, a special feature being the use of analogies; and they conclude by stating that the book will be useful to the advanced student as well as to the beginner. This is true, in our opinion, as the book is certainly very clear and instructive on many matters. It covers a considerable field apart from relativity proper, such as: Geometry, classical mechanics, Newtonian system, optics, electrodynamics, etc.

There is just one feature the reader should be aware of, and that is those statements made occasionally which seem to be in contradiction to accepted knowledge. This is because the author has treated the survey historically, and he has assumed that the reader knows the general trend of the subject well enough to accept a statement with reserve until he has penetrated further into the subject.

Referring to the aethor, the views respecting it would not perhaps meet with Sir O. Lodge's approval, but as we know nothing of this hypothetical medium apart from manifestations involving matter, one rather admires the book on this account.

The section dealing with the law of inertia of energy, particularly pages 232 to 237, is very interesting reading, and the argument given in support of this conception is very neat. Space will not permit us to quote here as much as we would like to.

On page 189 the wording: "having a carrier of light vibrations," would be better rendered by using the word *being*.

On page 235 "nuclei" and "protons" are stated (implied) as synonymous terms. While correct in the case of hydrogen, helium nuclei (He^{++}) are not protons, but this is only a result of glossing over those details that are not an essential feature of this book to treat. On page 235 we read: "Fundamentally, however, the discovery that when an atom is disintegrated the sum of the masses of the component parts is not equal to the mass of the original atom is of great importance." We agree absolutely; but the "discovery" is still hypothetical, as we know of no experiment which has revealed or weighed this difference. Pro. Born, however, makes this clear in the previous paragraph when dealing with radio-active disintegration.

Considering the size of the book—many pages having 480 words on them, there being about 285 pages of reading matter—the price, twelve shillings, is very reasonable. The publishers and the translator, Mr. Brose, are to be congratulated on the excellency of the publication. We thoroughly recommend the book as one of the best.

There appear to be comparatively few irregularities in the text. We note only two minor ones.

We have received a copy of "Chemical Reviews."

This new periodical was brought out in April, 1924, under the sponsorship of the American Chemical Society. This purely

scientific periodical has met with a very favourable reception.

It is devoted to articles of from twenty to fifty pages, consisting of reviews and essays, written by specialists and experts, summarizing existing knowledge on various subjects and phases of subjects of chemical interest.

Among the articles which are projected for Volume I are the essays which were written for the dedication of the Sterling Chemical Laboratory. These appear upon special arrangement with the authorities of Yale University. They are:

Some Factors Influencing Substitution in the Benzene Ring, by A. F. Holleman.

Some Recent Advances in the Field of Colloids, by The Svedberg.

Twenty-five Years of Research on the Yttrium Earths, by G. Urbain.

The Systematic Detection of the Rarer Chemical Elements, by A. A. Noyes.

Solid Solutions, by Giuseppe Bruni.

The Method of Willard Gibbs in Chemical Thermodynamics, by W. Lash Miller.

Atomic Weights and Isotopes, by T. W. Richards.

The Constitution of Polysaccharides, by J. C. Irving.

The Theory of Membrane Equilibria, by F. G. Donnan.

Organic Radicals, by Moses Gomberg.

The Quantum Theory of Chemical Affinity, by G. N. Lewis.

PUBLICATIONS RECEIVED.

The Tutorial Chemistry. Part II—Metals and Physical Chemistry.
G. H. Bailey, D.Sc. (Lond.), Ph. D. (Heidelberg). Edited by William Briggs, L.L.D., M.A., B.Sc., F.R.S.
Pages: viii + 511.
Fifth Edition, 1924.
London, University Tutorial Press, Ltd., High Street, New Oxford Street, W.C.
Price: 7s. 6d.

Cadmium, The Metallurgy, Properties and Uses.
Norman F. Budgen, Ph.D.M.Sc.
Pages.—xiv & 239. —1924.
London.—Messrs. Charlie Griffin & Co., Ltd., Exeter Street, Strand, W.C.2.
Price.—21/-.

New Patents.

This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

LATEST PATENT APPLICATIONS.

18739.—Cassella & Co., Ges. L.—Manufacturer of 4-amino-3-oxybenzene-1-arsinic acids. —Aug. 6th.

18740.—Cassella & Co., Ges. L.—Manufacture of arsinic acids of the aromatic series.—Aug. 6th.

SPECIFICATIONS PUBLISHED THIS WEEK.

219,420.—Smith, F.—Utilisation of waste lime from chemical works.

219,423.—New Jersey Zinc Co.—Manufacture of zinc oxide.

208,516.—Syndicat d'Etudes Chimiques.—Process for the recovery of nitrogen and acetone from molasses and vinasses.

219,599.—Kaunty, T.—Apparatus for liquefying and separating gases.

ABSTRACT PUBLISHED THIS WEEK.

217,715.—Synthetic Drugs.—Cassella & Co., Ges. L., Frankfurt-on-Main, Germany.

Alkyloxacridines are prepared by alkylating the corresponding oxyacridines in the presence of acid-binding substances, the acridine nitrogen not being alkylated in the process. From dioxyacridines may be obtained both mono- and di-alkyl derivatives. The products are of therapeutic value, arresting the growth, for instance, of diphtheria bacilli and streptococci. According to examples 3:6-dioxyacridine is methylated or ethylated with dimethyl or diethyl sulphate, 2:7-dimethyl-3:6-dioxyacridine is methylated with *p*-toluenesulphonic methylester, and 3:6-dioxyacridine is oxyethylated with ethylene-chlorhydrin with or without pressure; in each case the alkylation is performed in presence of caustic soda. The properties of the mono- and di-methyl- or ethyl-ethers and of the bisoxyethylether are given.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1/6 each.

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MANAGER,
CHEMICAL NEWS, 97, SHOE LANE, LONDON, E.C.4.

THE CHEMICAL NEWS,

VOL. CXXIX. No. 3360.

THE PREPARATION OF DERIVATIVES OF DEHYDROTHIOPARATOLUIDINE. PART II. ACETYL DEHYDROTHIOTOLUIDINE, BENZALDEHYDROTHIOTOLUIDINE, THE THIO UREA OF DEHYDROTHIOTOLUIDINE, DEHYDROTHIOTOLUIDINE DIBROMIDE, AND THE NITRATION OF DEHYDROTHIOTOLUIDINE.

By R. F. Hunter, A.R.C.Sc., M.S.Chim., F.C.S.

In Part I of this series of papers (Chem. News, 1924, CXXVIII, 88), it will be recalled that the nitration of dehydrothiotoluidine was discussed, and a peculiar observation was recorded as to the solubility of one of the products of nitration in alkali and ammonia.

The work on nitration has been re-examined, and it has been found that the alkali soluble substance which sometimes appears during the nitration of the thiazole is not a normal product of nitration, but is only produced when the reaction is allowed to proceed too vigorously and the real nitro compound is in fact insoluble in alkali.

The study of the preparation of derivatives of dehydrothiotoluidine has been continued, and the preparations of acetyl dehydrothiotoluidine, benzal dehydrothiotoluidine, the thio urea of dheydrothiotoluidine and dehydrothiotoluidine dibromide (1) as well as

$$[CH_3C_6H_3 < {}^{S}_{NBr} > CBr\ C_6H_4NH]_2$$

$$CH_3\ (NO_2)\ C_6H_2 < {}^{S}_{N} \geq C\ C_6H_4NH$$

the nitration of dehydrothiotoluidine and the preparation of nitro dehydrothiotoluidine to which the formula (2) is normally assigned, are recorded.

Acetyl dehydrothiotoluidine is best prepared by refluxing dehydrothiotoluidine with a mixture of acetic anhydride and glacial acetic acid for some time and pouring the resulting solution into water when the *acetyl derivative is precipitated* as a white substance which can be crystallised from ethyl acetate.

Benzal dehydrothiotoluidine is best prepared by adding theoretical benzal dehyde to a boiling alcoholic suspension or solution of dehydrothiotoluidine in alcohol, or spirit; on cooling the condensation product separates in yellow plates in nearly quantitative yield.

The thio urea of dehydrothiotoluidine is best prepared by refluxing dehydrothiotoluidine with carbon disulphide and alcohol containing a little potash for several hours, hydrogen sulphide is evolved, and on concentrating the solution by the removal of the bulk of mixed solvents, the thio urea crystallises out. It is a yellow crystalline substance, whose solubility in alcohol is low, and on warming with silver nitrate solution, splits off sulphur in the usual way with the production of black silver sulphide. *In alcoholic solution it yields a* brom addition product on bromination under the usual conditions (*loc cit*).

Dehydrothiotoluidine dibromide (1) is readily prepared by the bromination of an alcoholic solution of dehydrothiotoluidine, the brom thiazole is so obtained as a brown precipitate which is removed and freed from bromine by washing with water, alcohol and a little ether; the compound is formed by the addition of two atoms of bromine to the thiazole ring, the compound is readily reduced with the splitting off of halogen with reducing agents, but is stable to boiling water, unlike the brom acetyl derivative, which splits off bromine on treatment with hot water, and even on keeping in a dessicator for some time.

Regarding the nitration of dehydrothiotoluidine; by slowly adding the thiazole to fuming nitric acid at room temperature and pouring the solution into water, the brown *nitrate of the nitro compound was precipitated*. On collecting this and treating it with ammonia, change of colour takes place with the liberation of the free base, the colour change no doubt being quinonoid-benzenoid isomerisation of the usual type. Acidification of the alkaline filtrate does not produce a precipitate as recorded in a pre-

vious experiment. This peculiar observation was explained subsequently, however, when owing to the dehydrothiotoluidine used in a later experiment containing a trace of alcohol, a much more vigorous reaction ensued, and on pouring the nitro solution into water, two substances were precipitated, one of which was insoluble in alkali and was the normal nitro compound, the other being a brown substance soluble in alkali, precipitated by acidification of the alkaline solution and having a most unpleasant odour resembling that of the aminothiocresol obtained by alkali fusion of dehydrothiotoluidine. This alkali soluble substance only appears when the reaction is exceedingly vigorous and is not formed when the reaction is kept well under control, and is probably a base formed by the oxidative fission of the fused thiazole ring. Since the fused thiazole ring is readily ruptured by alkali fusion at the double bond between the nitrogen and carbon atoms of the hetero-cyclic ring, it is probably at this point that fission takes place in the very strongly oxidative medium. The ordinary nitro compouud is readily soluble in warm benzene and crystallises from this solvent in red brown crystals, the nitro compound also readily dissolves in glacial acetic acid, to give presumably a solution of the acetate, from which the free base is precipitated by the addition of alkalis.

EXPERIMENTAL.

Dehydrothiotoluidine was worked up from the commercial article by alcoholic extraction, followed by water precipitation, as previously described.

Acetyl dehydrothiotoluidine. 20 gms. of dehydrothiotoluidine are mixed with 20 ccs. of glacial acetic acid and 40 ccs. of acetic anhydride in a 500 cc. flask fitted with a reflux condenser and the mixture refluxed on a sand bath for ten minutes at its boiling point. The brown solution is poured into 400 ccs. of water, the white precipitate stirred and allowed to stand for two hours, filtered, washed with water and a little dilute alcohol.

Yield : quantitative.

The acetyl derivative can be crystallised from ethyl acetate, or taken up in alcohol and precipitated from the alcoholic solution with water. Crystallisation from alcohol is often difficult owing to tarring.

Benzaldehydrothiotoluidine. 100 gms. of the technical dehydrothiotoluidine are refluxed for ten minutes witb 500 ccs. of methylated spirit, the extract is filtered hot through a large filter paper into a litre round bottomed flask, the insoluble primuline stays on the filter paper. The extract is heated to boiling in the flask which is connected with a reflux condenser and heated on a boiling water bath. 18 ccs. of benzaldehyde (more or less than this quantity depending on the solubility of the thiazole in the alcohol) are run in with a little alcohol, and the mixture refluxed at the boiling point for ten minutes or more, poured into a beaker and the solution allowed to cool. The beaker and contents are allowed to stand overnigbt, and the yellow crystals of the condensation product filtered off and dried.

Yield : over 50 gms., but depends on the alcohol and the quality of the technical intermediate.

De-dehydrothiotoluidine thio. urea. 15 gms. of dehydrothiotoluidine obtained by precipitation of an alcoholic solution are dissolved in 200 ccs. of alcohol or more, 50 gms. of carbon disulphide are added and about 2 gms. of solid potash and the mixture refluxed in a litre flask fitted with a double surface condenser on a boiling water bath for four hours. The solution is transferred to a distilling flask, the bulk of solvent distilled off and cooled, the crystals filtered off and dried.

Yield : 12 gms.

Dehydrothiotoluidine dibromide. 10 gms. of dehydrothiotoluidine are dissolved in 150 ccs. of alcohol, the solution cooled and 3 ccs. of bromine slowly added drop by drop from a burette with stirring. The addition of bromine must be carried out carefully or else tarring may occur. The brown precipitate is allowed to stand half-an-hour and then filtered off. Washed with a little alcohol, much distilled water till free from bromine and finally with a little ether, and dried in a dessicator.

Nitration of dehydrothiotoluidine. 10 gms. of precipitated thiazole dried free from any alcohol, are gradually added to 70 ccs. of fuming nitric acid contained in a beaker, evolution of heat and nitrous fumes takes place. The beaker and contents are allowed to stand for an hour, and the solution then poured into 500 ccs. of cold

water. The brown precipitate is filtered off, washed with cold water, transferred to a beaker and treated with excess of dilute ammonia at a volume of about 300 ccs., the mixture stirred and warmed, filtered hot, washed and dried. A portion crystallised from benzene in brown red crystals.

The Chemical Laboratory,
Highbury New Park, N.5.

NOTES ON THE ACETYL VALUE OF FATS.

By J. C. Malpas.

The action of acetic anhydride on hydroxylated fatty acids can be expressed as follows :—

$C_{17}H_{32}(OH) \cdot COOH + (C_2H_3O)_2O =$
Ricinoleic acid   acetic anhydride
$C_{17}H_{32}(O \cdot C_2H_3O) \cdot C\ OH$
Acetyl-ricinoleic acid
$+ CH_3 \cdot COOH.$
acetic acid

At one time it was thought that the fatty acids which contain no hydroxyl group, like stearic, were unaffected by acetic anhydride. Then Lewkowitch discovered that pure stearic acid and other common fatty acids though having no -OH group did give marked acetyl values when treated by the original method of Benedikt's. The explanation given to this was by believing that on boiling the fatty acids with a large excess of acetic anhydride they were converted almost completely into anhydrides, thus :—

$$2C_{15}H_{31} \cdot COOH + (C_2H_3O)_2O = (C_{15}H_{31}CO)_2O + 2CH_3 \cdot COOH$$

When this acetylated product is boiled with water it is again converted to the acid.

$$(C_{15}H_{31}CO)_2O + H_2O = 2C_{15}H_{31} \cdot COOH,$$

But a small quantity is unchanged and not affected by the alkali in the cold. However, on boiling hydrolysis takes place and some of the alkali is neutralised which gives an apparent acetyl value that is without foundation. Therefore, Lewkowitsch proposed distilling off the acetic acid produced by saponification of the acetylated acids and estimate its quantity in the distillate.

The acetyl value is the number of milligrams of KOH required to neutralise the acetic acid produced by saponifying 1 gram of the fat after acetylation.

Recently I was reading some notes on this subject in *Chemie et Industrie*, by E. B. Elsbach and which originally appeared in "*Chem, Umschau, Fette, usw.*" They will be of interest here.

"The author of this article does not seem to be in the possession of the leading ideas, and recently some works have had in view the improvement of the definition, as well as the experimental determination of the acetyl value. At the outset the acetyl value was related to 1 gram of fatty matter acetylated.

Normann suggests a simpler method than that of Lewkowitsch. He distinguishes the acetyl value which coincides with a gram of the acetylated fat, from the hydroxyl value, which is returned as the original fatty substance. But in practice this process has given too much variation to be recommended.

The author first of all heats, from 2 to 5 grams of the fat to be analysed in a small round-bottomed flask, of which he gives an illustration. This heating is maintained at 100°, until the weight is constant, in a stream of carbon dioxide. One proceeds as follows to acetyate with 4 to 6 ccm. of acetic anhydride. The operation requires a half-hour under a reflux condenser. Then the excess of anhydride is driven off in a stream of carbon dioxide at a temperature of 100°, and reweigh.

If one expresses the difference of weights between the composition acetylated and the dry fat in percentage of the quantity fatty matter originally weighed = p, the author indicates formula as follows :—

Hydroxyl Value

$$= \frac{p \times 56{,}110}{42{,}016 \quad 100} = p \times 13{\cdot}354.$$

Acetyl Value

$$= p \times \frac{13{,}354}{1 \quad 0{\cdot}01p}$$

The formulas appear to us to give results from errors of conception. One would sooner in naming (p) the weights of original substance as (p_1) and the weights of dry substance as (p_2) the weights of dry substance acetylated would be then :—

Hydroxyl Value

$$= \frac{p_2 - p_1}{p} \times \frac{56,110}{42,016}$$

Acetyl Value

$$= \frac{p_2 - p_1}{p} \times \frac{56,110}{42,016} ,,$$

INSULIN.

[*Slightly abridged from the Report of the Lecture before the Royal Institution, March 28th, by Prof. HUGH MACLEAN, M.D., D.Sc.*]

No recent discovery in medical science has created so much interest, both in lay and in profesional circles, as the advent of insulin. The great importance of this discovery lies in the fact that through its agency a fresh outlook and a new hope have been opened up to the unfortunate sufferer from diabetes—an outlook in which despair and the prospect of almost certain death have given place to health and hope. From the humanitarian point of view, this itself is no mean achievement, but insulin has many interesting features besides its success in therapeutics, and the problem of its method of action presents an intellectual puzzle, which, from its complexity and obscurity, bids fair to engage our ablest scientific minds for many years to come.

Before discussing the results obtained from the use of insulin in diabetes, it is essential that certain points bearing on the metabolism of our foodstuffs* should be clearly understood, for diabetes is nothing more than an interference with the normal mechanism which burns up our food in the body. Unlike the healthy individual, the diabetic subject cannot utilise his food, and, in consequence, becomes thin and ill. He presents the curious anomaly that the more food he eats the thinner and weaker he becomes, for, as the result of the perverse process of metabolism from which he suffers, much of the food that he is unable to use is changed into poisonous bodies which circulate in the blood, and cause destruction of body tissue, soon to be followed by death.

Though one of the most important symptoms of diabetes is glycosuria,* or the presence of sugar in the urine, it is important to appreciate the fact that diabetes is a disease not of sugar or carbohydrate metabolism alone, but that the metabolism of all our foodstuffs is involved.

METABOLISM OF FOODSTUFFS IN THE BODY.

Our knowledge of the various changes which the different foodstuffs undergo in the body is unfortunately very meagre, but we know sufficient to enable us to understand the main points in diabetes. Our food consists largely of starchy material or carbohydrate, with a certain amount of fat, and a fair proportion of such products as meat, fish, eggs, and other related bodies known as proteins.

Fats and carbohydrates are used simply as fuel for the body, and as the result of their combustion, heat and energy are generated. Both ultimately produce end-products which are removed from the body largely in the expired air as water and carbon-dioxide. Proteins also supply heat and energy, but they are used for another purpose as well; they form the bricks for building up the waste tissues of the body. That part of the protein molecule which is not required for the renewal of waste tissue is utilised for the production of heat and energy, just as in the case of fats and carbohydrates.

If we endeavour to follow the course of carbohydrate metabolism in the body, we are at once presented with many difficulties, but a few main features are fairly clear. It is certain that starch, no matter in what form it is taken, is broken down in the intestinal canal by enzyme action into the simple sugar known as glucose. This glucose is then absorbed into the blood, and before getting into the general circulation, passes through the liver. If a great deal of glucose is present, the liver stores part of it for future use, and thus prevents an excessive amount of glucose from being present in the blood at one time. The storage substance which the liver forms from glucose is a starch-like body known as

glycogen. Though the chief depot for glycogen is the liver, a good deal is found in the muscles as well. This glycogen is gradually converted into sugar again in response to the requirements of the body, so that a certain amount of sugar is always available for oxidation by the tissue. There storage product besides glycogen is formed during sugar metabolism—the lactacidogen of Embden—but it is doubtful whether this substance, which appears to be of the nature of a compound of sugar and phosphoric acid, ever gives rise to sugar again in the muscles after it is formed. When sugar reaches the tissues it is burnt up and forms carbon-dioxide and water. Many investigations have been carried out in an endeavour to find the intermediate substances between these end-products and the larger sugar molecule, but of this phase of metabolism we know nothing with certainty.

Fat is also acted on by the intestinal juices and absorbed as free fatty acids and glycerin; it is largely stored as fat in the body. Before final oxidation, fat is broken down into a lower four-carbon fatty acid—oxybutyric acid—together with diacetic acid and acetone. These substances are then oxidised, forming the usual end-products, carbon-dioxide and water.

It is probable that both fat and carbohydrate have a definite and separate mechanism for metabolism, but that protein, on the other hand, does not possess a separate mechanism. When tissue waste is restored, the remaining protein is broken down into substances similar in nature to the intermediate products of sugar and fat metabolism, which are probably oxidised by the same mechanism as is used for fat and carbohydrate.

METABOLISM IN DIABETES.

In diabetes the carbohydrates are as usual hydrolysed to glucose in the intestinal tract, but after absorption the glucose tends to accumulate in the body, with the result that a certain amount of it is excreted in the urine. This excess of sugar in the body in diabetes depends on two causes. In the first place, the liver and muscles are unable to store the excess of sugar as glycogen, while in the second place, the tissues have lost to a great extent the power of oxidising sugar. The consequence is that a great deal of glucose is always present in the blood, resulting in a great waste of sugar through the kidneys. It is an interesting fact that one of the earliest manifestations of diabetes appears to be a lack of power on the part of the liver to store sugar as glycogen. This difficulty may be in evidence long before any symptoms of diabetes manifest themselves. In severe cases, oxidation of the sugar is also markedly interfered with, a phenomenon which depends on a lesion of the pancreas; this defective oxidation is most marked in the later stages of very severe diabetes. Generally speaking, sugar passes into the system of the diabetic and is largely passed out again without being utilised. Why this should be so is at present unknown, though various suggestions have been made.

The chemical researches of Fischer and of Irvine have demonstrated the existence of a more active form of glucose than the ordinary variety found in diabetic urine, and it has been surmised that this more active γ-glucose might be the form which the body requires for metabolism. If the body can utilise glucose only after it has been changed into the more active form, it is obvious that a defect in the mechanism responsible for this change would result in a condition similar to what we have in diabetes. The body would be supplied with a variety of sugar which it could not metabolise, with the result that this sugar would be excreted in the urine like any other foreign body. Attractive as this theory appears, it must be admitted that, so far no convincing evidence of the existence of γ-glucose in the body has been advanced.

With regard to the metabolism of fat in diabetes, it appears that the breaking down of the large fatty acid molecule goes on as usual to the stage of ketone bodies, but that these bodies fail to be oxidised; they therefore accumulate in the blood and are largely excreted in the urine.

As already explained, the oxidation of protein probably takes place partly along the path of carbohydrate metabolism, and partly along the path of fat metabolism. The result is that protein may give rise to both sugar and ketone bodies in the diabetic urine, about 60 per cent. of the amino acids of protein being capable of forming sugar, while 40 per cent. may be excreted as ketone bodies.

The total result of these changes in metabolism is that the urine of the diabetic subject frequently contains large amounts of glucose together with oxybutyric acid, diacetic acid, and acetone.

BLOOD SUGAR CHANGES IN THE NORMAL AND IN THE DIABETIC SUBJECT.

Some knowledge of the physiological changes which the blood sugar concentration undergoes in the body is essential in the study of diabetes. In the normal subject, when the blood is examined two or three hours after a meal, it is found to contain about 0·1 per cent. of glucose. As a rule the blood sugar does not sink appreciably lower than this in ordinary circumstances. After the ingestion of carbohydrate food, however, it gives to a maximum of about 0·16 to 0·18 per cent., and then quickly falls to the former level of about 0·1 per cent. Usually the maximum rise takes place within one-half to three-quarters of an hour after a meal, and generally the blood sugar content is found to be normal in about one and a half to two hours. These changes are best observed after a meal consisting of from forty to fifty grams of glucose. It might be thought that the early rise just described is due simply to increased absorption of sugar into the blood, and that the fall towards the normal level merely indicates that absorption is complete. This is by no means the case, as can be easily shown by experiment. Indeed, it would seem that absorption of sugar may be going on just as rapidly after the blood sugar falls to the normal level as it was when the blood sugar was at its maximum.

The explanation of the phenomenon appears to be that, after some absorption of sugar into the general circulation has taken place, a special mechanism comes into action which stores the sugar as glycogen and so reduces the amount in the blood; this mechanism resides chiefly in the liver. In connection with this storage action it is interesting to observe that it is generally quite impossible to raise the blood sugar concentration beyond 0·18 per cent. or so. No matter how much sugar is taken, no greater quantity than this will be found in the blood. Whenever the concentration reaches this point, the liver storage mechanism becomes so strongly developed as to prevent any further rise. The interest of this observation lies in the fact that whenever the blood sugar rises above 0·18 per cent. the kidneys begin to excrete sugar in the urine. Until this concentration is reached no sugar is excreted. The difficulty of raising the blood sugar beyond 0·18 per cent. or so indicates that glycosuria in the normal subject should be very difficult to produce as the result of ingesting large amounts of sugar, and experiments show that no sugar appears in the urine of the healthy subject however much sugar he eats.

From these statements it will be clear that the presence of sugar in the urine indicates that the blood sugar concentration is in the region of 0·18 per cent. or higher. Though the normal kidney does not excrete sugar until this concentration is reached in the blood, it sometimes happens that the kidney may leak and allow sugar to pass into the urine when the concentration in the blood is much lower than the figure given. This condition, which is fairly common, is known as renal glycosuria; obviously it has nothing whatever to do with diabetes. It gives rise to no symptoms and produces no bad effects.

(*To be Continued.*)

GENERAL NOTES.

THE AMERICAN CHEMICAL EXPOSITION.

Owing to some confusion which is believed to exist in a few quarters regarding the holding of the next chemical exposition an announcement has been sent out by the International Exposition Company, under whose management the Exposition of Chemical Industries has been held since 1915. Numerous inquiries have been received by the management which lead it to believe that many interested parties are of the opinion that there will be a chemical exposition this year. This is not the case. The next Exposition of Chemical Industries will be held from September 28th to October 3rd, 1925, at the Grand Central Palace, New York.

SEVERN BARRAGE.

The Government have decided to proceed at once with certain preliminary investigations in order to ascertain the feasibility of the scheme for using the tidal power of the River Severn for the production of electrical power hy the erection of a barrage across the river. Lord Parmoor, to whose scientific department (the Department of

Scientific and Industrial Research) the work has been entrusted, has already made arrangements to put it in hand.

The Lord President has appointed a Committee, constituted as follows, to supervise and direct the work :—

G. S. Albright, Esq., C.B.E., J.P. (Chairman), Professor A. H. Gibson, M.Inst.C.E., M.I.Mech.E., F.R.Ae.S., G. W. Lamplugh, Esq., F.R.S., Maurice Wilson, Esq., A.M.Inst.C.E., Dr. J. S. Flett, O.B.E., LL.D., F.R.S., *Director, Geological Survey* and Museum.

The feasibility of the Severn scheme turns first and foremost upon the possibility of finding satisfactory foundations for a barrage. Accordingly the first stage of the investigation will involve :—

(*a*) the study by the Geological Survey of the stratigraphical formations in the neighbourhood of the sites suggested for the erection of the barrage;

(*b*) taking preliminary soundings with a view to determining the contour of the river bed at the sites; and

(*c*) preliminary measurements of the flow of water at different states of the tide.

Meanwhile, two eminent consulting engineers, Sir Maurice Fitzmaurice, Kt., C.M.G., F.R.S., and Sir John Purser Griffith, Kt., M.A.I., M.Inst.C.E., have been *invited by the Lord President to submit* a joint report before the end of this year as to the possibility of constructing a barrage on one or more of the sites suggested on the assumption that safe foundations exist. The data which will be provided as a result of the geological and hydrographical investigations already mentioned will be placed at their disposal. The staff of the Geological Survey have already begun the enquiry entrusted to them, and their report will probably be ready for submission to the Committee before the end of September.

THE BRITISH ASSOCIATION.

[TORONTO MEETING.]

(*Continued from page 135.*)

Presidential address to Section B, by SIR ROBERT ROBERTSON, F.R.S., entitled *Chemistry and the State.*

Among other investigations on non-ferrous metals, those on 'season-cracking' of brass and its prevention and on the methods of extrusion, have been productive of useful results, and in connection with the Non-Ferrous Metals Research Association, work is in progress on the casting of brass to produce sounder ingots, on the die-casting of brass and bronze, and on the failure of lead cable sheathing by cracking.

During the war, the use of substitutes, the easing of specifications to increase output with safety, the examination of enemy ammunition, and the tracing of causes of failure and discovery of remedies provided a large field for investigation.

The other aspect of metallurgy of special interest to the State, that of minting, has a long history; from early times the need for a high and uniform standard of coinage, and the crime of debasing it, have been recognised. The difficulties that confronted the early assayers, without methods of quantitative analysis and with no fine balances, are apparent from the description of their methods, but it may perhaps be held that these needs as they became borne in on the early assayers and their frequent collaborators the alchemists, led the way to the appeal to weighing in chemical work.

As early as 928 A.D. laws were proclaimed by King Athelstan appointing 'mynteres' whose products were scrutinised at the trial of the pyx; later, in 1180, supervisors of the *coin manufactured by 'moneyers' were* appointed.

An official mention occurs in the reign of Edward I. of a Guild of Goldsmiths in London, which had, however, existed since 1180, in an Act providing for the assay of silver vessels by the Wardens of that craft. The earlier writings on the subject of assaying are those of Germans, of whom Queen Elizabeth brought over a number to introduce their methods and assist in the development of the resources of the country.

The course of testing seems to have been originally by means of the touchstone, supplemented much later by observing the effects of acid on the trace left by drawing the metal over the stone, the method of determination of density, the cupellation method, officially recognised by Henry II., and finally the wet method of analysis.

To safeguard the fineness of the coinage a King's Assayer was appointed in 1222,

a Master of the Mint manufacturing the coin under contract, and a Warden acting on behalf of the King. A Commission, having toured the Continental mints, reported in 1870 in favour of the present organisation of the Chancellor of the Exchequer being Master of the Mint in virtue of his office, a Deputy-Master being responsible for the administration, while the valuation of bullion and questions of assay are the duties of the Chemist and Assayer.

Many of the Mint officials have contributed largely to metallurgical knowledge. One of them, William Humphrey, in 1565, received the first patent for making brass, and a later one, Sir John Brattle, communicated work to the Royal Society shortly after its foundation on the oxidation of lead. Sir Isaac Newton when Warden is said to have himself conducted experiments on the composition of foreign coins. The melting-points of metals were studied in conjunction with Wedgwood by Alchorne, who was appointed Assay Master in 1789. From 1851 to 1870 several distinguished men of science, such as Hofmann, Graham (who in 1866 published a work on the effect of the occlusion of gases in metals), Miller, and Stenhouse, were officials of the Mint; but in 1870 it was considered preferable to conduct the chemical operations of assaying within the Mint itself, and Roberts-Austen, to whose pioneering work in metallurgy allusion has been made, was appointed. To his successor, Kirk Rose, are due many advances in knowledge of the precious metals. Thus, researches at the Mint have been directed to the investigation of metallic systems of gold with silver and other metals, the means of avoiding brittleness in gold coins, the electrolytic refining of gold, the mechanism of annealing of metals, the surface tension of solid and molten metals, as well as to improvements in the technique of the methods of assay.

REVENUE.

In reviewing the influence of our science in its application to Revenue questions, it is convenient to consider historically the substances on which the State has levied duties.

In the older tariffs, fixed charges were levied on goods considered as a whole, but a time arrived when the chemist was called in; it then became possible to make an assessment on the ground of a percentage. Uncertainty prevailed, therefore, as to the basis of taxation and gross adulteration flourished until scientific safeguards were introduced.

The chief substances with which the chemist is at present concerned from the Revenue point of view are the following :—(1) liquids containing alcohol; (2) tobacco; (3) sugar; (4) tea and cocoa; (5) dyestuffs, under the Dyestuffs (Import Regulation) Act, 1920; (6) substances under the Safeguarding of Industries Act, 1921.

(1) *Liquids containing Alcohol.*—On imported wine Richard I. imposed a duty, and as time went on complications were caused by the introduction of imposts for various purposes, including reprisals.

Acts were passed, as in the time of Charles II., for preventing the reprehensible practices of mixing wine, and vitiating it with other substances such as cider, sugar, herbs and vitriol; it is still forbidden to mix wines of different sorts.

The difficulty of distinguishing the strength of alcoholic liquids is apparent in the older enactments, when, for example, the Legislature describes brandy as a ' strong water perfectly made imported from beyond the sea,' and it was not until the reign of William III. that they were assessed, if not in proportion to their strength, at least in some relation thereto The first step was their separation into ' single ' and ' double ' proof, a rough and inconclusive one, but accounting for the use of a term still recognised as that on which the full statutory rate of duty is leviable.

For charging Revenue the gallon was first taken as a measure in 1825, but definite alcoholic strength was not introduced as a basis until 1860, under a treaty with France, while a little later, in 1862, Parliament distinguished between wines above and below 26 degrees of proof spirit, this figure being raised in 1886 to 30 degrees.

The want of some accurate method of test had been felt, and it is interesting to follow the gropings after a method for recognising a standard strength of alcohol. Thus observations on the surface tension of spirits were employed, for Postlethwaite in 1751 described as a mark of their being up to proof the length of time elapsing before bubbles disappear from the surface of the liquid contained in a glass tube which had

been shaken, but as he believed this method may be falsified, he recommended for more accurate work 'the essay instrument, or hydrostatical balance,' although for business men it would be sufficient to burn a measured quantity of the spirit in a metal cylindrical vessel immersed in cold water, and measure the remainder, which should be equal to half the original volume, if the spirits were proof. Although 'Boyle's bubble' had been described in 1675, and Moncony's aerometer in 1679, the first instrument generally adopted by the Revenue in 1730 was the hydrometer of Clarke, legalised in 1787. It is complicated, however, and its temperature correction by 'weather weights' was unsatisfactory, so that Parliament gave instructions for 'proper experiments to be made.'

At the request of the Government to the President of the Royal Society, Sir Charles Blagden (Secretary) and one of the clerks, Mr. George Gilpin, undertook to make experiments on the specific gravity of alcohol and water in varying proportion. These experiments, conducted with exemplary care and ability, were reported to the Royal Society in 1790, 1792 and 1794, and formed the basis for the tables of Sikes, whose hydrometer became the sole legal instrument in 1818, and is still in use. These tables remained legal for nearly a hundred years, but in 1916 were replaced by a new and extended set, prepared under the supervision of Sir Edward Thorpe at the Government Laboratory, whence also in the same year were issued comprehensive tables of spirit strengths for use with pyknometers, as these had shortly before been legalised for alternative use in the determination of alcohol. Both of these sets of tables were founded on the definition of proof spirit contained in the Act of George III., which is, that spirit which at the temperature of 51 degrees Fahr. weighs exactly 12-13 parts of an equalled measure of distilled water. In other words, it contains 49.28 parts by weight of pure alcohol and 50.72 parts by weight of distilled water.

As these tables refer only to alcohol-water mixtures, all disturbing substances must be removed before the strength of liquids is determined by hydrometer or pyknometer. The methods of freeing spirit in commercial articles from everything but water were investigated and laid down by the Government Laboratory in 1903 by Thorpe and Holmes.

From the point of view of trade it is highly important to have free use of ethyl alcohol, while from that of the Revenue it is essential to prevent the use of such duty-free spirit as a beverage. The most effective means to meet both requirements is to denature spirit which is to be delivered duty-free for trade purposes, and the question of the choice of a suitable denaturant is by no means easy. So long ago as 1856, the Government Chemist of the day, Mr. Phillips, proposed the addition of 10 per cent. of crude wood naphtha, and this has been found satisfactory for most purposes. The proposal was submitted to and approved by three well-known chemists of that day, Graham, Hofmann and Redwood, and this present year circumstances have necessitated the addition of a further nauseating ingredient, pyridine, in addition to mineral naphtha which was added in 1891. Mineralised methylated spirit which is sold without Revenue control, excepting that a licence is needed, contains this proportion, industrial methylated spirit 5 per cent., and power alcohol 2½ per cent. on the alcohol.

That some misunderstanding exists as to the facilities available for the use of alcohol in commerce in the United Kingdom appears from an article recently communicated to the Ottawa Section of the Society of Chemical Industry, in which are contrasted a considerable number of compositions approved in Canada with the apparently small number legalised in Great Britain. It might be well, therefore, briefly to indicate the position, in order to make clear the facilities that are available.

Mineralised methylated spirit consists of a mixture of 90 parts of alcohol, 9½ parts of wood naphtha, and half part of crude pyridine, together with 3/8th of 1 per cent. of mineral naphtha and 0.025 of an ounce of methyl violet dye in each 100 gallons of the mixture. It is sold under licence, but is otherwise unrestricted and duty-free.

Power methylated spirit, prepared in accordance with the following formula: 92 parts of alcohol, 5 parts of benzol, 0.5 part of crude pyridine, and 2.5 parts of wood naphtha, together with 0.025 of an ounce of Spirit Red III. dye in each 100 gallons of the mixture, is also sold without restric-

tion and freedom from duty when mixed with 25 per cent. of hydrocarbons or denatured ether or some other substance approved by the Commissioners of Customs and Excise.

Industrial methylated spirit, consisting of 95 per cent. of ethyl alcohol and 5 per cent. of wood naphtha, can be obtained for the arts and manufactures under the authority of the Board of Customs and Excise, under bond and certain not very onerous restrictions. Between three and four million bulk gallons are annually used for the making of such products as varnishes, linoleum, soap, solid medicinal extracts, ether, toilet preparations for external use, fine chemicals, photographic plates, dyes, surgical dressings, fireworks and many other purposes, including its use in the chemical laboratories of colleges, schools and works, and for preserving museum specimens. It is free from duty, but must not be present in an article capable of internal use, either as a beverage or a medicine.

Duty-free pure alcohol is allowed by the Board of Customs and Excise for scientific purposes to universities and public institutions for teaching and research, and specially denatured alcohol in arts and manufactures in which the use of the industrial methylated spirit is unsuitable.

The pure alcohol is allowed to colleges and public institutions for teaching and research purposes without any onerous conditions beyond the keeping of a stock account. Pure methyl alcohol is permitted by the Board of Customs and Excise to be used duty-free in arts and manufactures under regulations similar to those for industrial methylated spirit, and is largely used in the manufacture of formaldehyde, of methyl derivatives among dyestuffs and fine chemicals, and for the purpose of crystallisation.

The specially denatured alcohol, also free from duty, is allowed to manufacturers under restrictions compatible with the safety of the Revenue, a very wide choice of denaturants being permitted. When, as frequently happens, a suitable denaturant is found in some intermediate product, or acid used, or produced during the manufacturing operations, or when the alcohol is a constituent of some mixed solvent, permission is the more readily granted for its use. An example of progressive policy in the use of pure spirit is the recent decision of the Board of Customs and Excise to allow the use of pure ethyl alcohol denatured with 2 per cent. of pure methyl alcohol in the production of insulin, without onerous Excise restrictions. It is understood that the recent action of the Board of Customs and Excise has been received with satisfaction by the Association of British Chemical Manufacturers. The quantity of pure and specially denatured alcohol used during last year was about half-a-million gallons.

In the case of duty-paid spirits used for medical purposes, such as the preparation of tinctures, etc., and for scientific purposes in chemical laboratories, a rebate is allowed under the Finance Act of 1920, amounting to about 80 per cent. of the duty.

While the responsibility rests on the Board of Customs and Excise of safeguarding the illicit use of alcohol, chemists have been represented on such commissions as that of the Industrial Alcohol Committee of 1905, whose recommendations led to the Revenue Act of 1906, in which the proportion of wood naphtha was reduced to 5 per cent., permission being also given for the payment of an allowance of 5d. per proof gallon or about 8d. per bulk gallon on British spirits used for industrial purposes, in consideration of the increased cost of the spirits owing to Excise restrictions.

An important alcoholic liquid that has been liable to imposts from the time of Charles II. is beer, and it was charged acording to its strength or weakness as judged by the palate. After the application of science to brewing about the middle of the eighteenth century, the saccharometer was introduced, the pattern due to Bate being still in use for Revenue purposes. In 1850 an investigation made by the then Government Chemist, Mr. Phillips, and his assistant, Mr. Dobson, established a quantitative relationship between the proportion of alcohol produced in the process of fermentation and the solid matter previously in solution in the worts that had been fermented, and tables were prepared for use in determining the original gravity of the beer, *i.e.*, the specific gravity of the worts before fermentation had begun. These tables, after verification by Professors Graham, Hofmann and Redwood, were employed in the Revenue service until 1914, when they were superseded by revised ones

prepared by Sir Edward Thorpe and Dr. Horace T. Brown, these being rendered necessary mainly owing to the employment in brewing of many substitutes for malt unknown in the earlier days. As a rapid means for determining the original gravity the immersion refractometer is constantly in use in the Government Laboratory. This laboratory also furnished the scientific evidence for the Inland Revenue Act of 1880, which enabled brewers to use a great variety of substances for brewing.

(2) *Tobacco.*—Not long after its introduction Elizabeth imposed a small duty on tobacco, which under James I. met with not only his famous Counterblast, but an increased duty of 6s. 10d. a pound. Although Charles I. continued its repression and the Puritans regarded its use as 'profanity,' the snuff-box became in the time of Queen Anne a necessity of the fashionable world. A regular trade sprang up in preparing substitutes from various leaves, and numerous enactments proved incapable of preventing smuggling and adulteration. It was recognised that systematic chemical and microscopic examination had to be applied to the problems arising from this adulteration, and in 1843 a laboratory, which ultimately grew into the Government Laboratory, was erected to check it, with the result that this form of fraud was almost entirely stamped out. A strict watch is still maintained on all tobacco for home use or for export, both from the point of view of absence of foreign materials and of its hygroscopic condition, as the Revenue charge is based on the latter. Chemical control is exercised over the use of preservatives and the denaturing of tobacco before it can safely be allowed out of Revenue control.

(3) *Sugar.*—In the reign of James I. the importation of sugar was already sufficiently large to make it worth while to impose a duty on it, until at the beginning of the nineteenth century this amounted to 30s. a hundredweight. Before 1875. when the duty was abolished, disputes had arisen as to its proper assessment on the basis of description and character. When it again became dutiable in 1901 an extended classification was based on the polariscope scale, and sugars in numerous preparations had to be determined chemically. This has raised several difficult questions of chemical procedure especially when natural as well as added sugars are present.

(4) *Tea and Cocoa.*—Attempts were made in 1777 to stop the adulteration of tea with foreign and exhausted leaves and other matter, but it was not until 1875 that the Sale of Food and Drugs Act placed on the Revenue authorities the responsibility for examining tea on importation. This is done on an extended scale by the application of chemical, microscopic, and practical tests. There has been, however, no imposition of standards in the United Kingdom, as is the case in Canada and the United States.

The duty, and the drawback on the duty, on cocoa preparation has introduced chemical problems into the system of Revenue control, some of them of considerable difficulty, as, for example, those connected with the use of substitutes for the natural cocoa fat.

(5) *Dyestuffs, under the Dyestuffs Import Regulation Act,* 1920.—The importation of dyestuffs under this Act is controlled by a Dyestuffs Advisory Licensing Committee, on which distinguished chemists represent the science.

Importation of synthetic dyestuffs and intermediates is prohibited except under licence, and although the individual substances leave little room for doubt, more difficult questions come before the Government Laboratory in the case of substances containing a coloured ingredient.

(6) *Substances taken under Safeguarding of Industries Act,* 1921.—Part I. of this Act imposes an *ad valorem* duty on the products of certain 'Key' industries, of which the fine-chemical manufacturing trade is one. After the Act had passed into law, the Government Laboratory became concerned with the chemical aspect of that section which has gained notoriety through legal inquiries involving the precise significance of chemical and technical terms. But apart from such matters, many difficult chemical problems have arisen in determining the composition of the great variety of chemical substances imported. Thus it has proved a task of some magnitude to deal with about 8,000 subjects per annum, when their examination may include the quantitative determination of the ingredients of materials such as synthetic perfumes, photographic

developers, medicines, colloidal preparations, alkaloids, etc. The grade of a specified material has also frequently to be assessed, and this involves a special knowledge of its manufacture and use.

The effect of the war was generally to increase the amount of existing duties and to impose fresh ones. The former condition led to increased vigilance in the chemical control on account of the introduction of substitutes to replace the dutiable substances; the latter were imposed as a post-war condition and are described above. In connection with the war-time prohibition of exports, not only of munitions but practically of all useful commodities, the services of the Government Laboratory were required to decide as to the nature of about 20,000 substances, including cases in which the prohibited goods were skilfully disguised.

For all matters involving chemical advice the Board of Customs and Excise applies to the Department of the Government Chemist, who maintains on his staff for this section of the work a sufficient number of chemists and assistants to make the necessary investigations and deal with the chemical points at issue, as well as to carry out the necessary practical work, both in London and at several of the ports. This aspect of the work of the Government Laboratory involves a knowledge of Revenue law and precedent as well as an intimate acquaintance with a large range of chemical manufacture.

The importance of chemical control in safeguarding the Revenue is obvious. With increase in the number of subjects brought under supervision, the greater refinements and accuracy demanded, the investigation of new processes, and the amount of chemical work, the number of chemists is rapidly increasing.

(*To be continued.*)

CORRESPONDENCE.

BOOKS ON RARE AND PRECIOUS METALS.

To the Editor of THE CHEMICAL NEWS.

Dear Sir,

Could any of your readers supply me with a list of books published since 1915, dealing with the metallurgy and technology of rare and precious metals? I am anxious to purchase some recent works in this branch of science for the library of this University.

Yours, etc.,

WITOLD SIGISMOND SYROKAMSKY,
Asst. Prof. of the Ural University.
18, B. Sjezzaja Street,
Ekaterinburg,
Russia.

NOTICES OF BOOKS.

AUSTRALASIAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Report of the Sixteenth Meeting of the Australasian Association for the Advancement of Science, Wellington Meeting, January, 1923. Edited by W. R. B. Oliver, F.L.S., F.Z.S., pp. iv.+872. Association Office, Sydney, N.S.W., 1924.

The Presidential Address to Section B. (Chemistry) by Mr. H. G. Smith deals with the subject of "Some Chemical Characteristics of Australian Vegetation." Thirty odd years of research work on the chemistry of well-defined divisions of the Australian vegetation have shown this flora to possess many chemical characteristics with a systematic progression of characters. Chemical studies of plants have led to conclusions as to the evolutionary sequence of the members of certain groups. The genus *Eucalyptus* probably spread eastwards from N. & N.W. Australia and experienced varying soils and climate which are expressed by the responding characteristics of the genus. These results are expressed botanically by the timbers, the cotyledons and the leaf venation.

Recent bypotheses as to the relations of species have been formulated upon chemical data, and are borne out by botanical characters. *Eucalyptus* is essentially an oil-producing genius whose chemical characters emphasize a close relationship to *Angophora.* Pinene is the chief constituent of the oils of *Angophora* and the earliest group of the eucalypts. The pinene of *Angophora* has an almost specific rotation of about $[a]$ D $+44°$ and in *Eucalyptus* the pinenes may be either lævo or dextro rotatory reaching a maximum rotation in certain species of recent groups.

When growing under natural conditions the chemical characters of any one species of *Eucalptus* are comparatively constant, and each constituent follows the sequence of species increasingly until a maximum is reached. Extended work supports this stability, but one cannot help wondering whether the statement that this "as a corollary indicates that eucalypts not conforming to this chemical standard cannot be considered as identical species, although certain morphological characters may tend in the opposite direction" will receive universal unqualified approbation from systematic botanists.

Broadly speaking, eucalypts are distributed between two extremes of geological formation— silicious and basic, and cases are known where different species approach to a common boundary but do not intermingle. Many species, including those regarded as belonging to the oldest living type require a soil derived from rock containing upwards of 70 per cent. silica. The earliest leaves of members of this group, and those of most species of *Angophora* are coated with rubber, which may possibly be a polymerized hydrocarbon similar to that which produced the characteristic pinene of these early groups. Both substances have been derived from more simple bodies, and oxygenated oil contents are present only in very minute quantities—if at all. As the genus evolved oxygenated constituents became more pronounced, particularly cineole; and the formation of such constituents as the aromatic aldehydes, alcohols and esters is distinctly shown at this stage. Pinene still remained the chief terpene, and limonene and phellandrene did not appear until later. Botanical characters, particularly the leaf-venation, changed in agreement with the chemical characters. The characteristic terpene in the oils of the more recent groups is lævo-*a*-phellandrene (botanically indicated by the acutely spreading leaf-venations and the marginal veins being far removed from the edge of the leaf) which is usually associated with cineole, or piperitone, or terpineol and other oxygenated constituents in varying amounts. The phellandrene-oil-yielding groups appear to be the most recent in evolutionary sequence. About forty chemical constituents have been isolated from eucalyptus oils:—one ketone (piperitone); eleven alcohols including geraniol, terpineol, piperitol, and eudesmol; nine aldehydes including cuminal, aromadendral, cryptal, citral and citronellal; two phenols—tasmanol and australol; seven esters, including geranyl-acetate, terpinyl-acetate and butyl-butyrate; five terpenes—pinene, phellandrene, limonene, dipentene, and terpinene; a sesquiterpene (aromadendrene); a solid paraffin; cymene and cineole. The exploitation of the chemical constituents of eucalyptus oils has therefore become an important Australian industry. The evolution of a chemical character through a range of species until a maximum is reached can be seen in many instances. Geranyl-acetate reaches a maximum in *Eucalyptus Macarthuri;* citronellal in *E. citriodora;* citral in *E. Staigeriana;* cineol in *E. polybractea, E. Smithii* and *E. australiana;* piperitone in *E. dives;* lævorotatory pinene in *E. lævopinea;* dextrorotatory pinene in *E. dextropinea,* etc. The astringent exudations, kinos, of the earlier groups contain the crystalline body aromadendrin; as the genus evolved eudesmin appeared, and where one is present the other is found also. Eudesmin increases in amount through a range of species until the maximum of 10 per cent. is reached in the exudation from *E. hemiphloia* and closely related species. In later groups it is not produced.

Further papers in the proceedings of section B. are:—"A new view of atomic structure and the relationship of the chemical elements," by Professor F. P. Worley; "The essential oil of Leptospermum ericoides," by W. F. Short and C. W. Johnson; there are also abstracts of papers on "The determination of nitrogen in coal," by W. Donovan; "The hydrolysis of alkali cyanides," by Prof. F. P. Worley and R. W. Harman; "The surface tensions of aqueous solutions of certain aromatic sulphonic acids," by Prof. F. P. Worley and P. R. Parr; "The action of alkali cyanides on Gold," by Prof. F. P. Worley; "Some chemical components of the Ngaio," by F. H. McDowall; "The preparation of cyanacetic ester," by O. C. Stephens.

The subsection of Pharmacy contains the presidential address "Some chemical changes occurring in pharmaceutical preparations," by R. C. Cowley in which the main changes brought about on pharmaceutical preparations by the influence of light, heat,

ızymes, water and chemically allied sub-ances, and of *oxidation are dis-*ıssed. Other papers are "Liquor ucalpti Saponatus," by B. L. Stanton ıd A. T. Sissons, "Acidity or kalinity tests of some B.P. chemicals," by . J. Rosenblum, "The identification of the lid B.P. synthetics," by F. T. Parry; and ıstracts of papers on "The estimation of e more important pharmaceutical en-mes," by C. S. Callaghan, "A chemical ange in Liquor Arsenicalis B.P. on keep-g," by C. Delaney, and "The solubility aspirin in citrate and acetate solutions," F. Tattam.

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1. *Technique of Tissue Culture "in tro,"* pp. viii. + 80, text illustrated, 8°. 6 net.
2. *Tissue Culture in Relation to Growth d Differentiation,* pp. x. + 50, tt. iv., 8°, net.

By T. S. P. STRANGEWAYS. Cam-dge: W. Heffer & Sons, Ltd., 1924.

During the last two decades biological re-ırch has given increasing emphasis to the ıdy of the individual cell. As a result, ıny new methods have been evolved in ɔerimental cytology, of which one of the ıst promising is that of making hanging-ɔp cultures of cells and observing their ıaviour under varying conditions whilst ve. Work already performed on animal sue by this method may have an impor ıt bearing in the elucidation of cancer.

Many improvements have been made in technique of tissue-culture since Har-on's work in 1907, and in the first of the o books under notice full working details recent lines will be found. The setting and sterilization of the requisite appa-tus is described and exact instructions are ven for the preparation of the medium and e implanting of many kinds of tissue. ıe importance of using absolutely pure lts in the medium is emphasized and the tention of commercial chemists might be awn to the fact that apparently it is some-nes difficult to make a satisfactory saline cause pure salts are not readily obtain-le. The p.H. of the medium should be tween 7.4 and 7.8. All the glassware ed must be free from alkali or successful owth will not be obtained. Media con-taining glucose, serum, agar, etc., have not been dealt with as they offer no advantage over simple saline. The worker must ac-custom himself to aseptic methods of work and every step should be performed slowly and with care to eliminate risk of infection until aseptic habits are acquired. Methods of fixing and staining cultures are given, particularly of intra-vitam staining. Neutral red is recommended for the demonstration of cell contents other than mitochondria. For mitochondria janus green gives perfect results if it is the diethylsafranin azodime-thylanilin chloride janus green B of the Farb-werke Hoechst Co. Janus black is specific for mitochondria in living blood cells owing to the janus green it contains.

The second book gives a brief account of experiments and observations by methods described in the first book, and includes suggestions as to the possible significance of the results in relation to growth and differentiation of cells.

The various chapters deal with some of the matters on which tissue culture throws light: "Growth in Vitro," "Mitosis in Relation to Cell Physiology," "Redifferen-tiation," "Experimental Modification of the Cell," "Differentiation and Cellular Variation," and "Tissue Culture in Rela-tion to Inflammation and Repair." The author finds that cells cultivated in vitro may show amœboid migration followed either by reproduction or vegetation. No cell is ever wholly at rest, even when in the vegetative stage, and mitosis marks a paro-xysm of activity including every structure. Each cell should be regarded as an indivi-dual animal, which is independent of the organism as a whole. It is also suggested that chromosomes are structures that re-main inert during the turmoil of mitosis, and thus preserve their specific character and that chromation exercises its functions only when in solution. Doubt is thus thrown upon the assumption that chromosomes per-sist as structural entities throughout the life of the cell. Cells may apparently be modified and new types produced which "breed true" through an indefinite number of generations. Some startling results are described in the chapter on "Differentia-tion." Epidermal epithelial cells proliferat-ing in culture lose their structure, but if a sub-culture of connective tissue be added the cells commence to re-differentiate. The

close similarity in the behaviour of cells " in vitro " and in inflamed areas suggests that the cytological changes observed in each are the result of environic disturbance. If the reaction of the cell to abnormal conditions is too violent, the normal physico-chemical balance cannot be regained, and death ensues. Also, the sequence of events during the final stages of tissue repair in the body is parallel to that of tissue cultures when grafted into the living animal.

No worker engaged on problems dealing with living phenomena can afford to miss this most thoughtful and stimulating book. In fact, both books bear the stamp of very careful work and even the general reader who wishes to know the lines upon which modern work is developing outside his own subject ought to pay careful attention to both books as one leads to a greater appreciation of the other.

The current number of the *International Review of the Science and Practice of Agriculture* (N.S. II. No. 2, April-June, pp. viii. + 265-522, Rome, 1924) contains in addition to abstracts, original articles by P. Holdefleiss on " The Organisation of Agricultural Meteorology in Germany," H. Niklas on " The Importance of Soil Maps for Agriculture," K. Dorph-Petersen on " How Long Do the Various Seed Species Retain their Germination Power? ", J. L. Guimaraes on " The Sugar Cane in Brazil," L. Markoff on " Vine Cultivation and the Wine Industry of Jugo-Slavia"—a rèsumè of practical viticulture in Jugo-Slavia, C. Wriedt on " Formation in Breeding of Live Stock and Modern Research on Heredity " and by F. Samarini on " The Preparation of Hay by Means of Covered Silos of the Cremascan Type."

K. Dorph-Petersen's paper is particularly interesting, as since rumours of the germination of seeds after long intervals began to be rife, the problem of the longevity of seeds has engaged much attention, and definite experimental evidence on the subject is welcome. It was found that the more robust the seed, the better its power of germination after harvest, and the drier and cooler it was kept, the longer it would retain its power of germination. Leguminous seeds with a good germination had this but little altered after a lapse of 3 years, but then decreased, although *Trifolium repens*, *T. hybridum* and *Lotus corniculatus* germinated after 25 years.

Grass seeds with a high initial power of germination were nearly unaltered in 3 years but only a few species retained this power more than 7 or 8 years. " Roots " seeds (*Beta vulgaris, Brassica napus rapifera* and *B. campestris rapifera*) kept their germination power almost unaltered until the 9th year.

The germination power of Coniferous seeds became progressively less but seeds of *Pinus sylvestris* and *P. montana* germinated after 14 years. Also, in general, the speed of germination was found to decrease more rapidly than germination power.

The paper by F. Samarini is also of particular interest. In the Cremascan type of high, narrow, tubular silo, CO_2, produced by the intercellular respiration of the plant tissues that are compelled to live without atmospheric oxygen, is the chief factor affecting the preservation of forage. The action is analogous to that of alcoholic fermentation, as the CO_2 regulates and stops fermentation. Plants are not killed by CO_2 unless the amount in the air exceeds from 20—40%. Smaller amounts merely impede vital functions. Ten per cent. CO_2 aids the conservation of forage in silos as it reduces the heating of the mass and prevents the development of moulds. The principal aim in the Cremascan type of silo is to make the maximum use of the CO_2. If forage has been put into the silo when still green the cell-sap of the plants is exuded under pressure. The cell-sap is acid and forms a suitable medium for the growth of acid ferments in general. Such make their appearance and as a result of fermentation the sugars disappear almost entirely. This fermentation, however, is inhibited if the moisture content of the forage be reduced one-half, as bacteria will not then develop. Moreover, partial drying lowers the vital activity of the cells and the effect of CO_2 is more readily felt. No changes take place in the protein substances of partly dried silaged forage. Only 3·99% of the protein substances underwent retrogradation in four months as compared with 10—30% of change in the old open silo. Cremascan silos are no longer used for making acid forages, but only for the preparation of a special hay.

E. H. E.

New Patents.

This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

LATEST PATENT APPLICATIONS.

19250.—Ashcroft, E. A.—Treatment of sulphide ores, etc., Aug. 13th.

19063.—Casale, L.—Catalytic synthesis of ammonia. Aug. 11th.

19226.—Liebreich, E.—Production of solutions containing oxides of chromium, etc. Aug. 13th.

19445.—Synthetic Ammonia & Nitrates, Ltd.—Catalyst. Aug. 16th.

SPECIFICATIONS PUBLISHED THIS WEEK.

219,719.—American Smelting & Refining Co.—Process of producing metallic tin.

195,960.—Verein fur Chemische und Metallurgische Produktion.—Processes for the manufacture and production of pure sulphuric acid.

201,942.—Jucker & Co. Chemische Fabrik.—Recovering chromic salts from residues containing chrome.

200,511.—Farbwerke vorm. Meister, Lucius & Bruning.—Manufacture of carboxylic-acid chlorides.

ABSTRACT PUBLISHED THIS WEEK.

218,054.—Synthetic resins.—Bau, A., Hope House, Ramsbottom, Lancashire.

Phenol-aldehyde condensation products.—A synthetic resin, soluble in alcohol, is produced by condensing formaldehyde, a phenol and a polyoxyaldehyde in the presence of hydrochloric acid, so that the oxybenzylalcohol resulting from the interaction of the phenol and formaldehyde forms a glucoside, the whole polymerizing to a resin. In an example phenol, formaldehyde, glucose and concentrated hydrochloric acid are heated to 65-70° C. and the precipitated heavy oil washed with water and dried at a temperature not exceeding 55° C. to form the resin. Other suitable phenols are crude cresol, thymol carvacrol, pyrocatechin, guiacol and resorcein. The resins may be employed as electric insulators and their solutions for varnishes, and for impregnating woollen and hair textiles and woollen and fur felts. The Provisional Specification describes the use of a mineral acid generally.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1/6 each.

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SESSION 1924-25.

COMMENCING ON TUESDAY, 7th OCTOBER, 1924.

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JOHN J. JACKSON, DIRECTOR OF EDUCATION, CITY HALL, CARDIFF.

THE CHEMICAL NEWS,

VOL. CXXIX. No. 3361.

THE SODIUM CYCLE AND MODERN GEO-CHEMICAL PROBLEMS.

By J. H. Goodchild.

There is an idea abroad that it is possible to calculate the "Age of the Earth" from the sodium content of the sea. Rivers deliver x tons per annum, there are n tons in the existing ocean, then $\frac{n}{x}$ gives the number of years since water began to circulate on the surface of the globe. When various allowances have been made, a figure is arrived at of 90 million years.

To many *chemists this question of* "age" will seem an unimportant academic matter. At the same time, the methods employed belong to geochemistry. The age may not be important, but the outlook implied is important for all chemists. The question, "Is there a sodium cycle?" belongs *to the larger question: "On what* kind of Earth do the men, of 1924 imagine they are living?

In the foregoing calculation it is assumed that sodium is supplied to the rivers by decomposing "igneous rocks," and that these, without exception, come from a nether source into which no sodium can penetrate from either land or sea.

May it not be that this concepton of "igneous" does duty for all "invisible" sources?

Consider rapidly an analogy from the history of chemstry.

About 200 years ago Van Helmont set himself to discover, if possible, the source of the carbon fixed by plants. In contrast to animals the trees seemed to grow from nothing. The story goes that he performed a careful experiment. He weighed some slips of willow, weighed some soil, allowed the plants to grow, giving them the necessary water, and eventually noted the increase to about 30 times their original weight.

He reweighed the soil and found a slight loss. On burning the willows, he found that the weight of ash tallied pretty closely with the loss in weight of the soil. Whence had come the carbon? He reluctantly concluded that it must have come from the water. There was no "evidence" of any other source, nothing could be "seen."

Curiously enough, chemistry at the time *was entering on the Phlogiston phase and* had to go through it before the carbon cycle was discovered. (Van Helmont, inventor of the word "gas," had rather hard lines.)

Now Geology has had its "igneous" phase in the nineteenth century and the simplifying conception has made an enormous *amount of work possible.* A new day, however, is dawning through the volcanic cloud. Fuller knowledge of sold-liquid processes going on everywhere beneath our feet makes the old classifications into "igneous," "metamorphic" and "sedimentary" look altogether too clumsy. They are connected *psychologically with an outlook which* permits the most remarkable things to be said by able physicists and chemists on problems of the Earth. The escape of sodium from the sea, directly or indirectly, to re-appear as felspathic "igneous rock," is denied. It is said that *because sodium salts are soluble* they are not abstracted from the sea! This is all the more remarkable because the expression "abstracted" is used. Something engaged in *acting on* sea-water is thought of, but is regarded as incapable of *abstracting* sodium. Organisms abstract calcium, but for sodium there is no organism, no escape. The sea is a liquid contained in a receptacle with permanent, impermeable walls, a glorified evaporating basin which has not cracked during 90 million years of service.

Now, obviously, if sodium salts are soluble, wherever water can go, sodium will tend to go. This means that a strong base can be carried to every part of the *seemingly* solid land, that it can concentrate in those places where conditions exist for its fixation as insoluble compounds. We do not know all about these conditions, but we know, for instance, of permutite. Whatever the fact, the reasoning from the solubility is short-sighted. All that we know of metallic ores, of dolomitization, of replacement, of disintegrated rocks deep down and exposing enormous areas of surface, makes us disbelieve entirely in the walls of an uncracked evaporating basin. *Land and sea form* together something more like an "organism" which is capable of assimilating sodium into

its more permanent tissues, i.e., sodium may be abstracted from sea-water, indirectly, though there be no appreciable abstraction from the *open sea*.

The familiar distinction between land and sea has its *limitations* for the purposes of geodynamics. Just as Van Helmont was under the disabilities of his time as regards the diffuse source of carbon all around him, so the earlier geologists may have been led to the conception of "igneous rocks" through making the land too solid. Vulcanism may be but a violent incident which can no longer be allowed to blind us as regards the chemical implications of sedimentary deposits taken together with the complicated movements shown by mountain ranges. These do not to-day tell us so much of a "crust" as of an intricate "flowing" of substances about the globe. Out of this flow more or less definite land-forms appear and are again destroyed. Sometimes high temperature is a factor and the results are melodramatic, but the general idea of "igneous" has become a stumbling block in the description of the land-forms

If we can re-describe our world, then "igneous," metamorphic" and "sedimentary" may be replaceable. Phlogiston was given up when new language and new methods of measurement were tried, and "contorted schist" may be no better than "*dephlogisticated air.*"

The events attending the sinking of land below the sea, its being covered with sediment, its rise into mountains of complex structure, can be approached as a problem of Growth. One could take, say, Clarke's "Data of Geochemistry," and illustrate it, bearing in mind the methods and philosophy of Prof. d'Arcy Thompson's "Growth and Form."

Certain regions are helpful, but how they come to be so is too long a story for this article.

THE RELATIONSHIP BETWEEN MAGNETISM AND THERMO-JUNCTIONS.

By J. C. THOMPSON.

The theory of Magnetism as generally accepted is briefly that every atom is itself a little magnet. Under electrical or magnetic forces these little magnets arrange themselves in a uniform manner and produce a magnetic field. There are several theories which explain how each atom is a magnet. By some it is supposed that the electrons of the atom rotate round the nucleus in such a manner as to make the atom a magnet. Ampères theory that an electric current circulates round each molecule is regarded still as fundamentally correct.

There is another theory—that an electric current circulates not round each molecule but round a group of molecules.

The E.M.F. of thermojunctions must be due to the action between at least two molecules since it is produced between molecules of *different metals*.

A direct relationship between E.M.F. of thermojunctions and Magnetism would give reason to suppose that Magnetism too was caused by the interaction between at least two molecules.

Such a relationship is given here.

Let H = *Magnetic Susceptibility of a metal.*

Let P = Electro-Motive Power of a metal at 18°C measured against a substance having E.M.P 1.5 microvolts per degree less than lead.

Let A = Reciprocal of Atomic Volume of metal

$$\text{i.e. } \frac{\text{Density}}{\text{Atomic Weight}}$$

$$\text{Then } P = \frac{H + 7.52A}{5.52A}$$

when $\frac{H}{A}$ is greater than −2

$$\text{and } P = \frac{H + 1.63A}{.37A}$$

when $\frac{H}{A}$ is less than −2

When $\frac{H}{A}$ is equal to −2 both formulæ give the same result.

The above formulæ are theoretically deducted except for the constants which are obtained from graphs and must be con-

sidered as approximate. The theoretical deduction would take a book to explain. The value of P given by this formula is always positive, whereas the actual value of P may be positive or negative.

The reason for this is quite obvious from the theory.

Substance.	$\frac{H}{A}$	P By Formulae at 18°C	Pat 18°C
Iron	—	—	+11.3
Nickel	(about 154.5)	—	-21.1
Cobalt	94.3	18.4	-18.4
Pd	54	11.2	-10.5
Pt	12	3.6	-4.9
Ta	10.3	3.20	-2.47
Mg	7.8	2.8	-2.0
Al	6.5	2.6	-1.97
Sn	.4	1.5	-1.63
Cu	-.6	1.35	+1.46
Zn	-1.4	1.12	+1.27
Au	-1.5	1.10	+1.14
Ag	-2.0	1.00	+ .94
Pb	-2.2	1.5	-1.5
Cd	-2.2	1.6	+2.1
Hg	-2.8	3.2	-5.25
Sb	-17.0	41.7	+40.8
Bi	-30	76	-76

Notes on above table:

The value of H for Iron and to a smaller extent Nickel is doubtful.

The substances are arranged in order of $\frac{H}{A}$. It will be noticed that as $\frac{H}{A}$ decreases in value P decreases till Ag is reached and then increases.

Columns 2 and 3, P calculated by formula, and actual P are in agreement within limits of accuracy of data. In no case is difference between columns 2 and 3 large enough to alter order of P in metals.

The values of H are taken from Kaye and Labys' Tables.

The value of P at 18°C are calculated from values at 50°C given in Hadley's *Magnetism and Electricity* p 366 with aid of formula given there.

A is calculated from Density and Atomic Weight as given in Kaye and Laby's Tables.

An examination of values in H in Kaye and Laby's *Tables* will show that $\frac{H}{A}$ for Iron may be smaller for Iron than for Nickel and Cobalt.

THE STRUCTURE OF COPPER.

By Hawksworth Collins, B.A. (Camb.).

If the single force which causes Cu to be classified as a monad is not one of the two forces which cause it also to be reckoned a dyad, then it must be a triad. If such is the case, its atomic weight can be split up into as many parts, 39, 23, 7, 3, 1, as the element has valences in the following manner:—63 = 39 + 1 + 23. No other number between 48 & 79 inclusive can be split up in this manner into three parts, the unit occupying the second place as in many other cases lately given in *The Chemical News*.

The structure of the element would then be

K——H——Na = Ca——Na

This is the structure which was deduced for the element in *The Chemical News*, 1920, CXXI., 182, by the application of the five main principles in the constitution and structure of the elements.

It will now be proved to be correct quite independently by means of the laws of relative volume and of heat of formation.

Table I.

The Relative Volumes of Copper.

Cu	=	Na	+	Ca
5.23	=	0	+	5.23
7.13	=	1.9	+	5.23
9.54	=	9.54	+	0
14.77	=	9.54	+	5.23
9.07				

TABLE II.

Experimental Data illustrating the Volumes of Table I.

		Relative Volumes.	Theor S.G. at 15° C.	Obs. S.G.	
(198)	$CuAgI_2$	5.23 + 13.29 + 2(27.75)	5.729	5.7225	Rodwell
(199)	Cu_2AgI_3	2(5.23) + 13.29 + 3(27.75	5.738	5.7302	Rodwell
(200)	$Cu_2Ag_3I_5$	2(5.23) + 3(13.29) + 5(27.75)	5.72	5.7160	Rodwell
(201)	$Cu_2Ag_4I_6$	2(5.23) + 4(13.29) + 6(27.75)	5.72	5.7064	Rodwell
(202)	$Cu_2Ag_{12}I_{14}$	2(5.23) + 12(13.29) + 14(27.75)	5.71	5.6950	Rodwell
(203)	$Am_2CuCl_4 + 2H_2O$	2(23.87) + 5.23 + 4(15.085) + 2(14.03)	1.96	1.963	Schiff
(204)	CuS	5.23 + 15.53	4.58	4.59	Chem.Kal.
(205)	$Cu(NO_3)_2 + 6H_2O$	7.13 + 2(3.8 + 3 × 7.53) + 6(14.03)	2.047	2.047	Chem.Kal.
(206)	$K_2CuCl_4 + 2H_2O$	2(18.05) + 7.13 + 4(15.085) + 2(14.03)	2.423	2.426	Playfair & J.
(207)	$CuSiF_6 + 4H_2O$	7.13 + 13.02 + 6(5.42) + 4(14.03)	2.545	2.535	Topsoe
(208)	CuS	7.13 + 15.53	4.19	4.16	Nostrand
(208A)	Cu	7.13	8.836	8.838	Whitney
(209)	CuS	9.54 + 15.53	3.790	3.8	Nostrand
(210)	Cu_2Se	2(9.54) + 11.31	6.68	6.71	Nordenskiold
(211)	$CuSO_4$	9.54 + 15.53 + 2(7.53 + 2.51)	3.524	3.527	16° Pape
(212)	$CuCl_2 + 2H_2O$	9.54 + 2(15.085) + 2(14.03)	2.509	2.47 2.535	18° Bodeker Playfair & J.
(213)	CuI	9.54 + 27.75	5.095	4.41 5.7	Schiff Rodwell
(214)	$CuCl_2$	14.77 + 2(15.085)	3.0	3.054	Playfair & J.
(215)	$K_2Cu(SO_4)_2 + 6H_2O$	2(22.29) + 14.77 + 2(15.53 + 7.53 + 3 × 2.51) + 6(14.03)	2.154	2.164 2.137	4° Playfair Schiff
(216)	$Am_2Cu(C_2O_4)_2 + 2H_2O$	2(23.87) + 14.77 + 4(18.04) + 2(14.03)	1.911	1.923	Playfair & J.
(217)	$Cu(CH_3CO_2)_2$	14.77 + 2(22.18 + 18.04)	1.901	1.920	Schroder
(218)	$Pb(CH_3.CO_2)_2$	19.39 + 2(22.18 + 18.04)	3.246	3.238 — 3.264	Schroder
(219)	PbI_2	19.39 + 2(27.75)	6.14	6.12	Rodwell
(220)	Cu_2O	2(9.07) + 4.45	6.29	6.093	16.°5 Herapath
(221)	Cu_2S	2(9.07) + 10.51	5.52	5.521	Scheerer
(222)	$CuSO_4$	9.07 + 15.53 + 2(7.53 + 2.51)	3.56	3.572 3.530	Karsten Filhol
(223)	Cu	7.02	8.97	8.96	Berzelius

TABLE III.

	Heat of Formation of Copper.	Original Volume		Rel. Vol. in combination at 15° C.		Change of Volume
	-15500 = 120 × (-2.05) × 63	7.02	=	9.07	-	2.05
	-19080 = 120 × (-2.52) × 63	7.02	=	9.54	-	2.52
	-58590 = 120 × (-7.75) × 63	7.02	=	14.77	-	7.75
aq.	-64975					

TABLE IV.

Experimental Data illustrating Table III.

	Heat of Formation.		Theor.	Obs.	Corresponds in Table II. with No.
solid	Cu_2S -2(15500) + 49959	=	18959	20300	221
				18260 Thomsen	
solid	Cu_2O -2(15500) + 71515	=	40515	43800	220
				40810	
solid	CuCN -15500 - 6000	=	-21500	-20235	
				-22050	
solid	KCN 37274 - 6000	=	31274	30100	
				33450	
solid	CuI -19080 + 36227	=	17147	16260 T.	213
solid	Cu_2Se -2(19080) + 46380	=	8220	8000	210
solid	CuS - 19080 + 30681	=	11601	10100	209
solid	$CuCl_2$ - 58590 + 2(56786)	=	54982	51630 T.	214
aq.	$CuCl_2$ - 64975 + 2(63870)	=	62765	63200	
				62710 Thomsen	
solid	$CuBr_2$ - 58590 + 2(45244)	=	31898	32580	
aq.	$CuBr_2$ - 64975 + 2(52930)	=	40885	40830	
solid	CuO - 58590 + 96155	=	37565	37700	
				37160	
aq.	CuF_2 - 64975 + 2(77500)	=	90025	89600	
aq.	$Cu(NO_3)_2$ - 64975 + 2(-23300 + 3 x 32341)	=	82471	82230	
				81300	
aq	KNO_3 37274 - 23300 + 3(32341)	=	110997	110700	
aq.	$CuSO_4$ - 64975 + 6217 + 2(32341 + 96155)	=	198234	197500	

The two experimental values given for Cu_2S differ by 2000, and the two for Cu_2O by 3000, so that the inclusion of $CuCl_2$ in the above Table is permissible, although its theoretical H.F. differs from the experimental by about 3000. The percentage difference is, however, less than that of either of the other two.

SUMMARY.

As Cu sometimes acts like the monad Na, and at other times like the dyad Ca, the constitution NaCa, which was previously obtained for it, is particularly suitable. This constitution has now been proved to be correct:—

(I.) By the fact that four of the five combining volumes can be split up into parts in accordance with the law of relative volume. (1.9 and 9.54 have previously been shown to be volumes of Na, and the only other part remaining in three cases is 5.23).

(II.) By the fact that three of the combining volumes are supported by the law of heat of formation, and give the same original volume for the element.

GENERAL NOTES.

COAL AND POWER.

THE UTILISATION OF REFUSE FUELS.

The publication of "Coal and Power" by the Liberal Party is interesting as showing that it is beginning to be realised one of the most important national problems in Great Britain to-day is fuel economy and cheap electrical power.

"Coal and Power," however, from a scientific point of view, is a poor sort of production and much less important than many articles that have appeared in the press for years past, and the fact that the whole question is an extremely intricate and complicated one does not seem to be realised. It is not merely a question of erection of super-power stations, the cost of which is not even stated, and the inclusion of many different possibilities of fuel

economy is necessary for any really national and comprehensive scheme. One of the most obvious of these, for example, is the utilisaton for steam generation, along with coal or coke, of all the cheap and refuse fuels available, now thrown away generally at a considerable nett cost for carriage and the occupation of valuable land. Thus in the average chemical or other factory there is the general refuse, consisting of miscellaneous material such as paper, string, broken boxes, old sacks, straw, and general sweepings, of an average heat value of at least 3000-4000 B.Th.U. per lb., which should be collected systematically in galvanised iron bins, and utilised n the boiler house, in addition to the residues from extractions such as in the case of alkaloids, pharmaceutical products, vegetable dyes, and tannins. In very many cases also household refuse which has a heat value of 2000-5000 B.Th.U. per lb. after separating the more valuable material, ought to be burnt at the electricity stations, resulting in an evaporation of 1-1½ lbs. of water per lb. of refuse.

Coke breeze, both from gas works and coke ovens, is perhaps one of the best examples of the huge waste of refuse fuels, and this material has been thrown away in Great Britain to the extent of literally millions of tons. The average analysis is *something like 10,000 B.Th.U. per lb.*, 12-15 % moisture, and excellent results can be obtained with it by adopting modern methods, either alone or in conjunction with coal or coke.

The collieries themselves naturally provide a very considerable production of low grade fuel, in the shape of high ash material from the screens, pit dust, and washery settlings or "slurry." This latter has an average heating value of about 7500-8000 B.Th.U. per lb., with 28 % ash, and 20 % moisture, and can as usual all be usefully employed, only one example of the waste taking place almost everywhere.

The most difficult case of all is fine anthracite "duff" or "culm," which is quite impossible to burn under ordinary conditions. Although of course this fuel is *only available in certain districts, like* South Wales for example, it may be stated that the problem of burning it has been solved by the new "slot," elements of the "Turbine" forced draught furnace, in which for example the surface of a 6ft. 0ins. x 3ft. 0ins. grate of a "Lancashire" boiler contains over 2000 air slots. This subdivides the air blast to such an extent that the light material is not blown off the bars, whilst also it cannot fall through because of the special design of the air passages to the slots. Installations are now at work in South Wales evaporating as much as 5,000 airs lots. This sub-divides the air blast to such an extent that the light material is not blown off the bars, whilst also it cannot fall through because of the special design of the air passages to the slots. Installations are now at work in South Wales evaporating as much as 5,000 lbs. of water for a 3 ft. 0 ins. x 8 ft. 0 ins. standard "Lancashire" boiler, burning nothing but this extraordinarily difficult material.

The main point is that as far as national fuel economy is concerned, all kinds of refuse material, whether of low volatile and high ash content, or of a bulky character and little heating value, such as green wood refuse and material like spent tan, can be burnt in this way at the highest efficiency, especially when mixed with coal or coke, and the saving to be obtained in the average industrial establishment is generally 10.25% of the coke bill.

Another section of the refuse fuel question is coke oven and blast furnace gas, and it is stated the failure to utilise the latter to the full extent alone represents in Great Britain a loss of 1000,000 H.P.

CANADIAN CHEMICAL PRODUCTION, 1923.

The High Commissioner for Canada in London has received from the Dominion Bureau of Statistics at Ottawa, a preliminary estimate made by Mr. S. J. Cook, Chief of the Mining, Metallurgical and Chemical Branch, showing that the production of chemicals and allied products in Canadian factories last year reached a total value of more than $106,500,000.

Exports of Canadian products in this class were valued at 15.7 million dollars, and imports amounted to 26.1 million dollars in the same period. More than 124 million dollars' capital were invested in the concerns operating 466 plants and employment was furnished to about 14,600 employees. Salaries and wages paid totalled 17.8 million dollars, and the cost of materials used was about 52.9 million dollars. The value added by manufacturing or the difference between the selling value of the products made and the cost of

raw materials used in their manufacture was 53.5 million dollars. Increases were noted in the amount of capital employed, the number of employees, payments of salaries and wages, cost of materials and value of products, as well as in the value of imports and exports.

Nearly 82 per cent. of the 1923 chemical exports went to the United States, United Kingdom and Mexico in the order named, and nearly 13 per cent. was shipped to Newfoundland, Japan, British West Indies, Australia and New Zealand.

On the other side, more than 98 per cent. of Canada's import business in chemical products was from seven countries, with the United States leading and the United Kingdom next, followed by Germany, France, the Netherlands, Belgium and Switzerland. The remaining 2 per cent. of Canada's chemical import trade was drawn from more than a score of different countries.

VICKERS RESEARCH BUILDING AT THE BRITISH EMPIRE EXHIBITION

The Research Section of Vickers Exhibit at Wembley consists of a laboratory in which are shown in use some of the scientific apparatus and methods employed in Vickers factories. Although the laboratory has an area of 2170 square feet, all fully occupied with apparatus, any approach to a complete representation of the range of scientific laboratories has to deal with an enormous range of products, while its geographical distribution is co-extensive with that of the Vickers factories.

The scientific work required by such an industrial organism is of two kinds: on the one hand, the control of materials, processes and products; and on the other, research properly so-called. Research again, naturally divides itself into two categories, that which is directed towards a goal predetermined by the exigencies of production, such as an improved process or a new material, and that wsich aims, irrespective of questions of utility, at elucidating any obscure phenomena. The most successful investigators whether industrial or academic, are unanimous in declaring the research, and especially the type of research last described, cannot be omitted from the activities of a scientific worker without detriment to the quality of his output., It is a pabulum which plays a part in his mental growth not unlike that of the vitamines in his bodily growth. For this reason, although the laboratory attached to each factory has control as its most insistent responsibility, yet research is always being carried on; in particular, the Sheffield Works, dealing as they do on a vast scale with such a basic product as steel, are provided with a Metallurgical Research Department consisting of a suite of laboratories fully equipped to carry out investigations into all the complex phenomena, thermal, constitutional, magnetic, etc., which are encountered in the manufacture of metals in general, but of steel in particular.

"THE MECHANICAL BOY."

There is nothing so inexhaustible as the curiosity of the average boy. He wants, quite rightly, to know the why and the wherefore of everything, and sometimes he asks questions which are embarrassingly difficult to answer. It will please parents, as well as the rising generation, therefore, to hear that at last a weekly paper has appeared — "The Mechanical Boy" (published by Percival Marshall & Co., 66, Farringdon St., E.,C.4. Weekly 3d.)—which should keep the reader interested and absorbed for a long time. The first number, besides articles on "Wireless in Aeroplanes" and "Science at Scotland Yard." contaius the opening chapters of a serial by Edgar Wallace, dealing with adventures which follow the opening up of wireless communication with an amazing planet. Other articles include "The World's Largest Ships," "A Turbo-Electric Locomotive," and "Making a Loud Speaker," and cover a variety of subjects from wireless and engineering to simple constructional work, The paper is illustrated by unusual and striking photographs, and is one which will delight any boy.

BRITISH DYES CLAIM.

A brochure which tells the story of the British dyestuffs industry has just been issued by the British Dyestuffs Corporation Limited for the benefit of visitors to the British Empire Exhibition at Wembley. The triumphs and vicissitudes of the industry from Perkin's discovery of the first

artificial dye in 1856 are reviewed at length, and the need for research is especially emphasised. It is pointed out that whereas in 1902 only twenty-one per cent. of the chemists in the British chemical industry held high University degrees (as against sixty-nine per cent. in the German industry) to-day the British Dyestuffs Corporation alone employs one hundred and twenty-five chemists, of whom eighty-three per cent. hold such degrees.

"It is freely admitted by those competent to judge," the writer concludes, "that eighty per cent. of the dyes used in this country are now British made, which is an entire reversal of the position from 1885 onwards. The British dyestuffs industry can therefore claim with all modesty that *it has made good*. This is not to say it has reached its ultimate goal. Such criticism as now exists is mainly directed towards price questions, but the trend of the general average of prices has consistently been downwards. What is important is not so much where we stand as which way we are going; and the direction is right. The last few years have been years of acute and world-wide trade depression, and the advantages to be secured by regular and bulk production cannot of course be obtained until trade becomes normal. Rome was not built in a day, nor will be the British dyestuffs industry, but what has already been done is in every way an earnest of abundant and final success."

EPITHELIOMATOUS (SKIN) ULCERATION AS AFFECTING PITCH AND TAR WORKERS.

H.M. Chief Inspector of Factories directs attention to the fact that some Pitch and Tar Workers develop small warts or ulcers on the skin of the face, arms, and very frequently in the neighbourhood of the private parts of the body, especially on the scrotum, and it is these that may grow into the serious condition.

If a wart or ulcer appears on any part of skin, medical attention should be sought *at once*, so that a doctor can advise the proper treatment.

All warts or ulcers do not necessarily grow into cancers, but they may do so, and are therefore best removed. This can be done quite simply. There is little fear of cancer developing under 10 years of employment and if the worker is under 35 years of age.

The only treatment known to be successful at the present time is to remove the growth completely by operation, and therefore the smaller it is the more easily can this be done, and the sooner it is treated the greater the chance of success. Delay may make all the difference between success and failure.

Fortunately, the form of cancer which is the most curable by operation, so that it *will not recur*, is *cancer of the skin*.

It is, therefore, very important to keep the skin healthy and the pores of the skin open. The only way of keeping the skin healthy is by frequent washing with soap and water.

The International Institute of Agriculture has published, in the monthly International Crop Report for August, a summary of the cereal crop situation derived from official information to hand from various countries. Although crop estimates from several important producing countries are still unavailable, the aggregate of the ascertained data will supply a fair indication of the present aspect of matters in the northern hemisphere. Exclusive of Russia, the countries where data of yields are available usually produce about 80 % of the wheat, 70 % of the oats, 60 % of the barley and about 55 % of the rye, grown in the northern hemisphere.

The yields of this year, according to the ascertained data of northern hemisphere countries, may be taken as about an average, though generally indicating decreases, of more or less importance, when compared with those of 1923.

The percentage of this year's production, in the countries brought into account, as compared with that of 1923 and of the previous five years' average, results in the following index-numbers:

Index numbers relating to 1924 yields.

	Compared with 1923.	Compared with the 1918-1922 average.
Wheat	87.5	98.8
Rye	83.9	82.6
Barley	91.0	99.9
Oats	95.2	103.6

The most recent information as to the southern hemisphere crops, telegraphed to the International Institute of Agriculture, announces that the condition of the cereal crops in Argentina is good, with an increase

of 3 % in the area sown with wheat, and a slight decrease in that under oats, barley and rye. In the Union of South Africa the weather was not favourable for the crops. The wheat crop is in excellent condition in Western Australia, but in New South Wales, Victoria and South Australia there was still need for good rains.

INSULIN.

[*Slightly abridged from the Report of the Lecture before the Royal Institution, March 28th, by Prof.* HUGH MACLEAN, *M.D., D.Sc.*

Continued from Page 144.

In diabetes the glycosuria is always due to an increased amount of sugar in the blood —a hyperglycæmia—and the changes in blood sugar concentration after eating starch or sugar are very different from those in the normal subject. If 50 grams of glucose are given to a diabetic subject, the rise in blood sugar is much higher than in the normal, and it continues high for a much longer period. Generally, of course, it happens that the blood sugar in the diabetic is much higher to begin with than it is in the normal subject, but it may often be reduced by appropriate dieting to the region of 0·1 per cent., and when this is done and sugar is taken, the blood sugar soon shoots over the 0·18 per cent. mark and often reaches 0·3 per cent. or more, at which high level it may remain for hours.

Glycosuria not Diabetes.

Though glycosuria constitutes an important symptom of diabetes, it must be celarly understood that the finding of even large amounts of sugar in the urine does not mean that diabetes is present. When glycosuria results from a leakage of sugar through the kidney, the condition is obviously of little or no importance, as already explained. *Temporary glycosuria* is not infrequently produced as the result of such conditions as mental excitement and fear. The explanation that has been suggested by physiologists to account for the increase of blood sugar caused by fear, is, that under primitive conditions some degree of fear was generally a preliminary to active muscular exertion of a defensive nature, and that the sugar was provided as fuel for the production of the required energy. Again, it is very common to find sugar in the urine of students after an examination. An interesting observation bearing on this point was reported some years ago by certain American observers. They examined the urines of a number of male students after an examination and found sugar in 18 per cent. of them. On extending the experiment to female students, contrary to expectation, no such result was in evidence, but since these latter were all much younger than the males, it is probable that the irresponsibility of youth rather than any fundaemntal lack of emotion was the cause of the difference. Glycosuria also appears as the result of taking various drugs and is not very uncommon in elderly patients who practise the belief so widely prevalent that rejuvenation and restoration of bodily and mental vigour may be obtained by the *indigestion of large amounts of thyroid* gland extract. Another cause of glycosuria not infrequently encountered is the excessive use of alcohol. After long dinners in which alcohol may play but a moderate part, glucose is frequently found in the urine on the following day. All these conditions are dependent on a temporary hyperglycæmia, but they disappear whenever the condition giving rise to them is removed. This glycosuria must not be regarded as of a diabetic nature.

Chief Symptoms of Typical Diabetes.

Along with the blood and urine changes described above, the diabetic suffers from general weakness, marked emaciation, great mental depression, thirst, hunger, and a very great tendency to the onset of a most serious condition associated with drowsiness and ultimately resulting in unconsciousness and death; this latter state is the fatal condition known as diabetic coma. It is liable to appear sooner or later in every case of severe diabetes, and, apart from accidental complications, is the usual cause of death in the diabetic subject.

Though this is the general course in typical diabetes, it must be admitted that the progress of the malady varies much in different individuals, and that many varieties of the disease, from a chronic slowly progressive type to what might almost be called fulminating diabetes, are encountered. Before the advent of insulin it was quite the exception for a patient suffering from well-marked diabetes to live for more than five or six years, though some-

times this period *could* be extended by careful dieting. This class of case is easily recognised and represents typical diabetes mellitus.

Another variety of so-called diabetes is by no means uncommon in middle-aged and elderly individuals. The patient may feel quite fit, or more frequently he complains of being somewhat out of sorts, with weakening of the limbs and a feeling of tiredness and lack of energy. On examination of the urine a large amount of sugar is found, but no ketone bodies are present. Unlike the true diabetic, there is no emaciation; indeed such a patient tends to get excessively fat. The presence of this condition is not incompatible with the enjoyment of more or less good health for very many years, during which sugar is continually passed, and frequently there does not appear to be any progressive tendency on the part of the disease. In such cases thee is no danger whatever of coma intervening, and it is obvious that the condition differs essentially from that of true diabetes. Indeed, the patient is not really suffering from diabetes at all, but from a well-marked and persistent glycosuria; his urine contains none of the toxic metabolic products characteristic of diabetes.

What happens in this type of case is that the liver has to a large extent lost the power to store sugar as glycogen, with the result that there is constantly a more or less excessive amount of sugar present in the blood, giving rise to glycosuria. Unlike what occurs in true diabetes, where a definite defect in the pancreas is present, there is here apparently no difficulty in oxidising sugar or fat in the tissues, hence the absence of ketone bodies in the urine. The constant excess of blood sugar probably stimulates the pancreas to produce more insulin, with the result that a good deal of this sugar is stored as fat in the same manner as the diabetic patient treated with insulin tends to put on fat. Occasionally, though not very frequently, this type of persistent glycosuria develops after many years into a true diabetes. This somewhat rare contingency appears to depend on the fact that the large amount of blood sugar constantly present stimulates the pancreatic cells to an over-activity which sometimes results in exhaustion. While true diabetes is probably always associated with a panceatic elsion, the type of so-called diabetes just described appears to be dependent on a disturbance of the liver. Though, in true diabetes, the liver also fails to store sugar, yet this is but one part of the condition; the most important point is that oxidation of sugar and other foodstuffs is defective. In the glycosuria of elderly individuals the defect appears to be limited to the liver.

The Cause of Diabetes.

The older observers appear to have been impressed by the frequency with which patients dying from diabetes showed definite lesions in the pancreas, and the older literature contained many statements emphasising this point. It was not, however, until 1889 that the relationship of the pancreas to diabetes was definitely established. In that year, von Mering and Kinkowski, in an epoch-making paper, showed that the removal of the pancreas from an animal resulted in a condition which was practically the same as severe human diabetes. Removal of part of the gland might or might not produce glycosuria, according to the amount of healthy tissue left behind, but complete extirpation was followed in every case by intense symptoms and a fatal termination in coma within a few weeks. Evidence was obtained that the result was not dependent on the loss of the ordinary pancreatic tissue, and it is now generally accepted that certain small islands of special cells found in the pancreas—the Islets of Langerhans—are connected with carbohydrate metabolism, and that their destruction or removal results in diabetes. These important experiment constitute the foundation on which all subsequent advances in our knowledge of diabetes, including the discovey of insulin, are based.

Attempts to Obtain Pancreative Extracts for the Treatment of Diabetes.

The discovery that destruction or removal of the pancreas* in animals gave rise to diabetes at once suggested the idea that this disease might be successfully treated by giving pancreas or pancreas extract to the patient. It was obvious that the pancreas must contain some active principle which was necessary to prevent diabetes, and the natural inference was that if this substance could be supplied to the diabetic the symptoms of diabetes would disappear. At first, fresh pancreas or various extracts of the gland were given by mouth, but without any apparent effect. Later, various special preparations were tried by injection, but the

results, though by no means always negative, were variable and unsatisfactory. It may with confidence be said that practically every investigator interested in diabetes has at some time or other tried the effect of pancreatic extracts.

It soon became clear that no effect whatever was produced when the preparations were given by mouth, but several observers had quite marked results when hypodermic or intravenous administration was used. Thus, for example, Zuelzer in 1908 prepared an extract which he injected into diabetic patients, with the result that, though no change was made in the diet, the sugar and ketone bodies previously present in the urine were much reduced, or indeed in some cases disappeared altogether. At the same time the patients improved in general health. The method was, however, given up on account of the frequency with which injections were followed by more or less serious disturbances in the patients, some of whom became very ill, while others showed high fever, rigors and prostration. Zuelzer's product was prepared from the pancreas by the use of alcohol. He assumed that the active principle was easily destroyed by the pancreatic ferment, and took the view that this might be prevented by treatment with alcohol. Later, Scott, working in America on somewhat similar lines, obtained a preparation which was definitely active, though rather weak and inconstant. Various observers had somewhat similar experiences, but nobody was able to prepare a trustworthy non-toxic substance for clinical use in diabetes, and a few years ago it seems as if the problem was insoluble. The disappointing results of so many investigators tended to substantiate the impression that further work on the problem was not likely to produce results, and our earlier hope of being able to treat diabetes successfully by pancreatic extracts had to a large extent vanished.

This was really the position when Banting took up the subject. Banting adopted the view propounded by many earlier investigators that the trypsin of the pancreas destroyed the internal secretion or hormone necessary for normal carbohydrate metabolism, and that the failure to obtain an active substance depended on this digestive action of trypsin. The difficulty was to devise some means by which this destructive action of trypsin during extraction of the pancreatic tissue could be avoided. It was well known to physiologists that the ordinary pancreatic tissue which secretes enzymes for the digestion of food underwent degeneration after ligature of the pancreatic duct, while on the other hand the islets of Langerhans were not affected. Banting therefore tied the duct in an animal, and after several weeks removed the degenerated pancreas. If the theory mentioned was correct, an exact of this pancreas should contain an active substance for the treatment of diabetes, since no digestive enzymes would be present. This actually proved to be the case, for a simple saline extract of this pancreas when injected into a diabetic animal lowered the blood sugar and reduced the amount of sugar passed in the urine.

This result was exceedingly interesting, but its practical application on a large scale was obviously impossible. Fortunately, however, it was soon found that the initial tying of the duct was unnecessary, for further experiment on the lines of Zuelzer's work showed that quite active preparations could be obtained from the normal pancreas. Ox pancreas was macerated as soon as possible after the death of the animal and left standing for several hours in 95 per cent. alcohol. The mixture was then filtered and the clear fluid obtained evaporated to dryness by means of a current of warm air. The residue was then dissolved in saline and used for injection. To this active substance Banting gave the name "Insulin."

It is not quite certain whether Banting's original view is correct, but this is of little importance from the practical point of view. Banting's success was largely dependent on the ease with which blood sugar can now be estimated, for it was essential in judging of the effect of insulin on animals that blood sugar estimations should be carried out at frequent intervals. Some years ago this was practically impossible, but now blood sugar may be estimated in the same animal every few minutes if necessary. To Banting belongs the credit of having prepared an active extract of pancreas suitable for the treatment of diabetes, but it must not be forgotten that this great achievement was rendered possible only by the laborious work of many earlier observers. Banting's final triumph was no doubt largely brought about as the result of modern developments

in bio-chemical methods, but, taking everything into consideration, it still remains a mystery why insulin was not isolated many years ago.

As was the case with all former investigators, Banting's earlier products frequently gave rise to more or less alarming symptoms when injected into patients, so attempts were made to obtain a purer substance. These attempts were successful, and samples of insulin were soon prepared which possessed little or no toxic effects. The present methods of manufacture depends on the isolation of a crude product by fractional precipitation of pancreatic extract with alcohol; this impure body is treated with picric acid, and insulin picrate precipitated, from which a fairly pure substance suitable for clinical work is obtained. This method requires the use of large amounts of alcohol and is somewhat tedious and expensive; also, it takes several days to complete the extraction and preparation of the insulin. Quite recently, Dodds, at the Middlesex Hospital, worked out a process for the isolation of insulin which possesses many advantages over the usual method in vogue. The principal of this method is based on the earlier observation by Dudley, that insulin could be most conveniently separated as the picrate. In the modification suggested by Dodds, the fresh pancreas is thoroughly ground up with solid picric acid, thus converting the insulin directly to picrate, and so reducing the time during which tryptic action may occur. By this process the old tedious filtration of the alcoholic extract is rendered unnecessary. The pancreas-picric acid creamy mixture is treated with acetone, which dissolves out the insulin picrate. The picrate is then purified on the usual lines. Not only is this method more expeditious, but also it actually gives a higher yield of insulin.

(To be continued.)

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CORRESPONDENCE.

JOINT COMMITTEE FOR THE STANDARDISATION OF SCIENTIFIC GLASSWARE.

To the Editor of THE CHEMICAL NEWS.

Dear Sir,—The Joint Committee for the Standardisation of Scientific Glassware is a committee, working under the aegis of the Institute of Chemistry, having members representing the users, manufacturers, dealers and Government Departments interested in scientific glassware. The Committee was formed to consider questions relating to the standarisation of scientific glassware. A list of members is given in the report on Units of Volume.

The Committee have given very careful consideration to the fundamental question of units of volume and desire to call your attention to the enclosed report, which embodies their recommendations. It is hoped that these recommendations will be accepted generally by those responsible for the instruction of students.

A further question to which the Committee have devoted considerable time is the accuracy of volumetric glassware. It was considered that two grades of volumetric glassware, and two only, are desirable and necessary, namely:—

CLASS A. OR STANDARD APPARATUS.

This must be of the highest accuracy reasonably attainable, of best quality materials and workmanship, and each vessel should be tested and approved by an im-

partial institution before being accepted as of standard grade. The National Physical Laboratory is the appropriate institution in this country for carrying out the tests.

CLASS B. OR COMMERCIAL GRADE APPARATUS.

This is a cheaper quality apparatus for general use, but guaranteed by the manufactur to conform with definitely recognised limits of accuracy and other necessary requirements.

The specification for Class B. apparatus must necessarily be less stringent than for Class A. apparatus, and should, for the sake of economy, make the minimum demands on the manufacturer consistent with satisfactory service for work in which commercial grade apparatus may reasonably be employed.

The Committee consider that the regulation for the Class A. Tests and Class B. Tests on volumetric glassware laid down by the National Physical Laboratory form a satisfactory basis for the two grades of apparatus. These regulations are contained in a Laboratory test pamphlet* which has recently been revised and the National Physical Laboratory has afforded the Committee the fullest opportunity of co-operating in the revision.

The manufacturers' representatives on the Committee have agreed to supply, in addition to standard Class A apparatus tested at the National Physical Laboratory, Class B apparatus guaranteed by themselves. They will undertake to replace any article so guaranteed and found not to fulfil the requirements of the National Physical Laboratory regulations for Class B apparatus, with apparatus tested at the National Physical Laboratory and bearing the Laboratory mark signifying that it complies with the Class B requirements. No charge will be made by the manufacturers for any such replacements.

The sale, purchase or use of volumetric apparatus inferior in quality to Class B apparatus is detrimental to the best interests of all concerned, and the Committee hope to see the elimination of all such inferior apparatus. Candidates for examination, in particular, should be entitled to put confidence in the accuracy of the apparatus with which they are provided, and if they are given inferior apparatus they are liable to suffer grave injustice in the assessment of their work by reason of errors which lie outside the scope of their own manipulation.

The success of the Committee's efforts must ultimately depend upon the action taken by purchasers of volumetric glassware. The Committee would therefore urge upon educational authorities and institutions the desirability, when they are purchasing volumetric glassware, of specifying either

(a) That the apparatus must have passed the Class A tests at the National Physical Laboratory and be accompanied with a Laboratory certificate.

or (b) That the apparatus must have passed the Class A tests at the National Physical Laboratory—certificate of corrections not required.

or (c) That the apparatus must have passed the Class B tests at the National Laboratory.

or (d) That the apparatus must be guaranteed by the vendor to comply with the National Physical Laboratory regulations for Class B tests.

The alternative adopted, will, of course, depend upon the purpose for which the apparatus is required.

The Joint Committee fully realise that for elementary teaching purposes economy in initial outlay on apparatus is a necessity. They feel confident, however, that, subject to a satisfactory demand, manufacturers will be able to supply guaranteed Class B. apparatus at prices consistent with reasonable economy. They also believe that it will be found ultimately more economical for advanced work and research, for which apparatus of doubtful accuracy cannot be tolerated and calibration is essential, to purchase tested Class A. apparatus rather than to purchase untested aparatus and invarably *carry out a calibration after* purchase.

Finally, the Committee would urge most strongly that under no circumstances should orders for volumetric glassware be placed without definite limits of error being specified, as failure to do so tends to en-

* Copies of this pamphlet may be obtained, gratis, on application to the Director, National Physical Laboratory, Teddington, Middlesex.

courage the production of inferior apparatus in which quality and accuracy are unduly sacrificed for cheapness. Some of the cheaper calibrated apparatus is known to be so inaccurate as to lead to grave errors even in the most simple determinations. The Committee believe it will be found that the simplest and most satisfactory way of specifying limits will be to refer to the National Physical Laboratory tests as indicated previously.

Yours faithfully,

G. W. MARLOW,
Secretary to the Joint Committee.

30, *Russell Sq., W.C.*1.

LITERARY INTELLIGENCE.

Messrs. Longmans, Green & Co. will shortly publish for the Manchester University Press a work entitled "An Introduction to the Study of Recent Corals," by Sidney J. Hickson, Professor of Zoology in the University of Manchester.

It is difficult for students at home who have only skeletal parts to handle to realise that in their natural haunts the corals are living, breathing, and feeding animals or plants, and no study can be complete or satisfactory unless some knowledge can be gained of the structure by which they capture and digest their food, the colours they display in life, and the means by which they propagate their kind. A description of the *structure of the soft parts of the coral* and of its appearance when alive is given wherever possigle in the description of the Genera. The accurate determination of corals is not only of importance for the student of pure science, but it has its economic value in the study of the problems of distribution and variation of the coral reefs of the world.

The work is fully illustrated.

NOTICES OF BOOKS.

Handbook to the Exhibition of Pure Science arranged by the Royal Society.

The Exhibition of Pure Science forms a part of the scheme for the Government participation in the British Empire Exhibition. In the majority of cases the exhibits are shown by scientists actually engaged in the work, supplemented by instruments loaned by some of the leading firms of scientific apparatus makers. Wherever possible demonstrations are given of the apparatus in use.

The handbook describing these is arranged in two parts. The first consists of a series of articles by well-known authorities, giving a clear indication of the present state of scientific achievement. The second part is a descriptive catalogue of the exhibits, numbered to correspond with the cards displayed.

The Royal Society has also arranged some of the exhibits in the Chemical Hall in the Palace of Industry. Descriptions of these are also contained in the catalogue, but the fact that they are exhibited elsewhere is indicated.

The handbook is obtainable from Messrs. Denny, 163a, Strand, W.C.2, price 1s., or post free 1s. 3d.

Skinners' Cotton Trade Directory, 1924, has just been issued by Messrs. Thomas Skinner & Co., Gresham House, London, E.C.2, price 25s.

It contains information of value to those connected in any way with this industry. The directory is well arranged and maintains the standard of its predecessors.

Kolloidchemie and Biologie, by VON PROF. FREUNDLICH. Pp. 47. Dresden and Leipzig: Verlay von Theodor Steinkopff. 1924. 50 cents.

This little volume is intended as a kind of third edition of Prof. Freundlich's *Kapillarchemie und Physiologie*. It includes the subject matter of recent lecture upon various physico-chemical phenomena observed in connection with plant and animal life.

The author directs the attention of biologists to the achievements of colloid chemistry, laying stress on recent applications.

Studies in Occult Chemistry and Physics. Vo. 1, by G. E. SUTCLIFFE. Pp. XIX. 202. Madras: Theosophical Publishing House, Adyar. 1923.

This interesting work is largely concerned with the exposition of concepts which are associated with Eastern thought. These, it is urged, are receiving more and more confirmation from experimental work, and the author cites the case of relativity as an example.

The postulate that weight and inertia are identical, which is a fundamental portion of the theory of Einstein, is said to be confirmed by the results of occult research. An important distinction between the teaching of Western science and that of eastern occultism is stated to be that according to the western view the total radiant energy per unit volume of ether which is in temperature equilibrium with matter is *finite*, whereas according to the occult tenets it is *infinite*.

The author has attempted to build a kind of bridge between the study of occultism and that which he associates with western science.

As this is only Vol. 1, it may be confidently hoped that future volumes will further contribute to the geneal correlation of facts and theories, for the author has relied upon exact mathematical calculations in support of his contentions.

Is It Good English? by JOHN O'LONDON. Pp. 176. London: George Newnes Ltd., Southampton St., Strand. 1924. Price 2s.

John O'London has issued in book form selections from the many dialogues on good English that have appeared in his *Weekly*. He maintains that the writing of good English follows from clear thinking rather than the system of rules called Grammar which youth loathes and maturity forgets. The correct and incorrect expressions and the usages of many words and phrases are carefully explained and exemplified, and for those of us who spend most of our time in the laboratory his help on many points is very welcome, although the volume is primarily intended for literary and not scientific readers.

Among the questions considered are the correct use of "the former" and "the latter"—phrases often used carelessly; "no" and "not any"; use of foreign words freaks of composition, etc.

Two of the many other matters are worthy of more than passing note.

In order to avoid a split infinitive, writers occasionally distort or weaken their sentences. The author contends that the splitting of an infinitive may be admitted when the alternative construction is ambiguous or artificial. An example appeared in a recent London University examination paper, in which the expression "to exactly neutralise" occurs, which, though objectionable to purists, is in reality a stronger expression as it stands.

J.G.F.D.

The Conference on Bureaux of Information and "Special" Libraries was held from September 5th to 8th, at High Leigh, Hoddesdon, Hertfordshire. Many interesting topics, including papers on abstracting and recording, were discussed.

BOOKS RECEIVED.

Aniline and its Derivatives, by P. H. GROGGINS, B.Sc. Pp. VI. + 256. London: Chapman & Hall, 11, Henrietta Street, Covent Garden, W.C.2. 1924. 18s. net.

Bulletins issued by the Department of The Interior. United States Geological Survey:—

Additional Ground-Water Supplies for the City of Enid Oklahoma, by COLEMAN RENICK. Pp. 15 to 26.

Bureau of Mines.

Silver in Chloride Volatilization, by C. M. M. BOUTOM, W. C. RIDDELL and L. H. DUSCHAK. Pp. IV. + 56.

Mineral Resources of the United States 1921, by G. F. Loughlin. Pp. IV. + 130a.

Tests of Marine Boilers, by Henry Kreisinger, John Blizard, A. R. Mumford, B. J. Cross, W. R. Argyle, and R. A. Sherman. Pp. XIV. + 309.

Geologic Literature on North America 1785-1918, by John M. Nickles. Pp. 1 to 658.

Weights and Measures. Pp. 1 to 153.

New Patents.

This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

Latest Patent Applications.

19655—Blackburn, H. W.—Manufacture of ammonia. August 19.

19829—Bregeat, J. H.—Recovery of volatile solvents. August 21.

19740—Soc. Chemiques des Usines du Rhone.—Reduction of halogenated carbides. August 20.

Specifications Published This Week.

220043—Potter, H. V., and Damard Lacquer Co., Ltd.—Phenolaldehyde condensation products.

216478.—Naugatuck Chemical Co.—Process for preparing a reaction production of acetaldehyde and aniline.

Abstract Published This Week.

218458—Alkylamines.—Green, A. G., and Ozley, H. F., Crumpsall Wale Chemical Works, Blackley, and British Dyestuffs Corporation, Ltd., 70, Spring Gardens, both in Manchester.

Methyl- or ethyl-amines are separated from a mixture with ammonia and other gases, such as results from the catalytic interaction of methyl or ethyl alcohol with ammonia, by passing the mixture through solid ammonium chloride bathed in methyl or ethyl alcohol. The ammonium chloride is contained in a tower or towers, beneath which the alcohol is boiled and above which is a reflux condenser. In the case of the ethylamines, the mono di- and tri-bodies react with the ammonium chloride with evolution of ammonia to form the corresponding hydrochlorides, which dissolve in the alcohol and are separated by liberating the bases and fractionally distilling them. Of the methylamines, the tri-body is not affected by the treatment and issues from the tower with the residual gases and is removed therefrom by compression and cooling; the mono- and di-bodies dissolve in the methyl alcohol and are separated by allowing the hydrochloride of the monomethylamine to crystallie out and evaporation of the filtrate to obtain the dimethylamine hydrochloride.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1/6 each.

SURPLUS SCIENTIFIC BOOKS, some of which are rare and valuable, and many of which were formerly the property of the late Sir William Crookes.—Apply for list and prices to The Manager, *The Chemical News*, Ltd., 97, Shoe Lane, E.C.4.

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THE CHEMICAL NEWS,

VOL. CXXIX. No. 3362.

ELUDE SUR LA CHOLESTERINE.

PAR PROFESSOR STEFÂN MINOVICI, PH.D. (BERLIN) F.C.S.

Le sujet que j'ai l'honneur d'esquisser est un résumé des connaissances actuelles sur la constitution chemique de la cholestérine et de son rôle dans l'organisme.

On connaissaitous ce corps qui se rencontre en quantité plus qu'appréciable tant dans l'organisme que dans celui végétal.

Un tel corps ne pouvait ne pas former l'objet d'une étude, tant au point de vue chimique qu'a celui physiologique.

Inspiré par les classiques travaux sur la composition chemique du cerveau, faits par un de vos illustres compatriotes, *Thudichum* (Die chemishe konstitution des Getierms des Menschen u der Thiere Tuburgen von F. Pietzcker (1901),—j'ai eu aussi l'occasion de m'occuper de la cholestérine qui est un des corps qui se trouve en quantité appréciable dans le cerveau, soit dans la proportion de 27-30 grammes.

Les essais datent depuis longtemps, mais ils se sont multipliés surtout à partir du commencement de ce siècle avec les progrès de la chimie organique. Bien que jusqua'à ce jour on n'ait pu encore résoudre définitivement la constitution de la cholestérine, les remarquables recherches de *Windaus* (*Abderhalden*: Handbuch der biologischen Srbertsmethoden Abt. I. Teil 6.) et de ses collaborateurs, nous ont mis cependant sur une voie plus ou moins proche.

La cause des difficultés réside en premier lieu dans le fait que c'est un corps riche en C (27) qui s'enchainent (sans discussion) dans la molécule; 2) dans le fait que les corps, aux noyaux hydrogénés, auquels appartient aussi la cholestérine, n'ont pas été synthétisés jusqu'à présent, et 3) que dans les essais faits pour établir son édifice moléculaire, on obtient souvent de nombreux produits de transformation qu'on ne peut isoler ou obtenir sous des formes cristallines aptes à être analysées.

Sa formule brute, établie pour la premiére fois par *Berthelot* [Ann. chim. phys., *56*.51. (1856), était $C_{26}H_{44}O$, tandis qu'aujourd'hui, après les analyses microchimiques de Pregl et *Lieb*, on donne comme certain qu'elle contient $C_{27}H_{46}O$ (*Reinitzer*). [Monoctsh f. chem. 9. 421 (1908).]

Le fait qu'elle ne contient qu'un seul atome d'oxygène, a conduit à établir avant tout la fonction de cet atome. Les recherches ont démontré qu'il est attaché comme oxydrile, et la preuve en ets dans les éthers obtenus par *Berthelot* [c.c.] avec divers acides organiques. Il résulte de ces recherches que la cholestérine est un alcool.

En 1904, *Diels* et *Abderhalden* [Ber. 37 3099 (1904); ,) Ann 146 176 (1868)] ont réussi à oxyder la cholestérine, en la chauffant avec de l'oxyde de cuivre entre 280-300°. Ils ont obtenu une cétone, le cholestéron. Il résulte de ce fait que la cholestérine est un alcool secondaire.

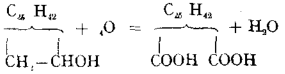
Mais la cholestérine contient aussi une double liaison — comme *Wislicenus* et *Moldenhauser* l'ont démontré les premiers—vu que la cholestérine additionne très facilement une molécule de brome et même une d'acide chlorhydrique.

$$\overbrace{\underset{\text{CHOH}}{|}\qquad\underset{\text{CH}=\text{CH}_2}{|}}^{C_{24}\ H_{41}}$$

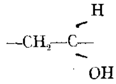
Par la réduction du chlorure de cholestérine *Mauthuver* u *Tuidor: Monatsh 15*. 87 1894)] par l'alcool amylique et de sodium, on obtient le *cholesten*, ($C_{27}H_{46}$); tandis que par l'hydrogénation de la cholestérine par voie catalytique on a pu introduire deux hydrogènes, obtenant le *di-dydro-cholestérine* *Willstätter* u. *Haff*. Ber *45* 1472 (1912)] ou l'alcool secondaire saturé de formule $C_{27}H_{48}O$, qui peut passer facilement dans l'hydrocarbure saturé de la série de la cholestérine, le *cholestan* [*Diels* u. *Linn*: Ber. *41*. 548 (1908); *Mourthner*: *Monatsh. 30*. 638 (1909)] $C_{27}H_{48}$. Ce cholestan contient 8 atomes d'hydrogène en moins que la paraffine respective saturée, $C_{27}H_{56}$. Ce manque de 8 atomes d'hydrogène doit être conditionné par l'existence dans la molécule du cholestan de quatre noyaux hydrogénés. Le premier noyau, celui qui contient aussi le groupe alcoolique, peut se déduire, facilement, comme l'ont démontré *Diels* et *Abderhalden* par oxydation avec du hypobromite de potassium, quand on obtient un acide di-carbonique sans que la double liaison soit influencée.

Il se produit donc une scision dans le groupe hydroxilique, sans que la molécule se

scinde dans d'autres constituants. Le processus peut être formulé de la manière suivante :



ce qui prouve que l'on trouve dans la cholestérine le groupe cyclique suivant :



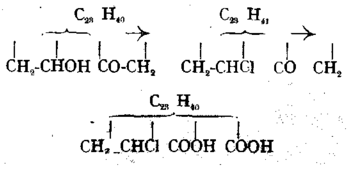
et qui, par oxydation, donne naissance à deux carboxyles.

Outre ce groupe cyclique saturé, on trouve encore un deuxième, mais non saturé, qui contient la double liaison et qui a eté caractérisé *par Windaus et Stein* [Ber., *37.*, 3699 (1940); *36* (3753) 1903; *37* 3702—3707 (1904)].

Comme point de départ dans ces recherches, les auteurs se sont servis des composés nitriques de la cholestérine et de ses dérivés, comme par exemple du nitroacétate de cholestéril, $C_{27}H_{44}(NO_2)$ $(OOCCH_3)$ et du chlorure de cholesteryl, $C_{27}H_{44}(NO_2)$ (Cl); et même de nitrocholestène : $C_{27}H_{44}(NO_2)$.

De même les dérivés nitriques de la cholestérine donnent, avec la poudre de zinc et l'acide acétique, des cétones saturées, en même temps qu'avec le groupe alcoolique obtenu par la saponification de l'éther, un corps par conséquent possédant une fonction alcoolique et une cétonique, le *cholesta-nonol*: [*Windaus*: Ber., *36.* 3753 1903)] $C_{25}H_{44}$ [CHOH] (CO).

Celui-ci peut échanger l'oxydrile par du chlore, au moyen du pentachlorure de phosphore, et enfin, il peut s'oxyder par l'acide azotique en se transformant en un acide chlor-di-carbonique.

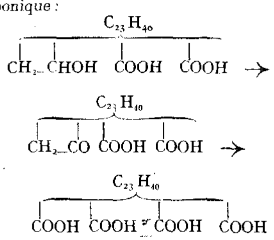


L'obtention de cet acide di-carbonique, qui reste dans les mêmes rapports, près du chlor-cholestanon, comme l'acide camphorique près du camphre, prouve que le groupe cétonique dans le chlorecholestanon, se trouve dans un noyau hydrogéné et près du groupe CH_2.

Il résulte de ces faits que la double liaison d'ou naquit le groupe cétonique se trouve aussi dans un cycle.

On peut prouver très facilement que ce deuxième noyau est différent du premier qui contient le groupe hydroxilique.

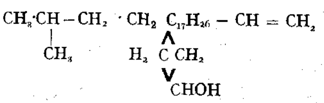
Si on introduit dans l'acide chlor-di-carbonique, dont on a parlé plus haut, à la place du chlore le groupe hydroxylique, on obtient un oxy-acide, lequel, oxydé au moyen de l'acide chromique, se transforme en un acide cétonique, et celui-ci, par la scission du noyau, passe dans l'acide tetra-*carbonique :*



Il en résulte que le groupe hydroxylique et la double liaison, se trouvent dans la *cholestérine, dans deux noyaux hydrogéniés* différents.

Les premières recherches qui ont été faites sur la cholestérine ont permis de constater dans sa molécule la présence d'un noyau alicyclique, — compris entre deux groupes méthyléniques—d'un groupe vinylique, et d'un groupe isoamylique.

En tenant compte de ces faits, *Windaus* [Ber., *42.* 3771, (1909); Arch. Pharm. *246* 134 (1908); Ber. *50* 134 (1917); *Abderhalden*: Handbuch der biologischen Arbeitsmeth. Abl. I, Teil 6] a proposé, en 1919, la formule de constitution suivante :



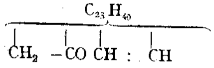
en supposant un groupe vinylique final.

Considérant d'une part qu'a l'occasion de la formation des composés nitriques, deux atomes d'hydrogène se séparent de la molécule de la cholestérine et qu'il se forme des dérivés deshydrogénés, et d'autre part, comparant la formation de ces produits deshydrogénés comme la transformation de l'acroléine-aniline dans la quinoléine, et que le groupe vinylique final, par l'enlèvement, de deux atomes d'hydrogène, peut être transformé en un groupe cyclique.

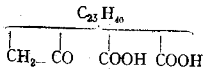
Le fait que dans la cholestérine on doit trouver le même arrangement des atomes de C que dans les dérivés nitriques et dans leurs produits de transformations, nous ets prouvé par le cholestanon-ol et le hétéro-cholestanon, qui, par réduction, conduit au même hydrocarbure saturé, le cholestan, qu'on peut obtenir directement en partant aussi de la cholestérine. Par conséquent les deux noyaux cycliques qu'on a pu déterminer dans la molécule du cholestanon-ol, se trouvent aussi dans la cholestérine.

Vu la constation faite que dans la cholestérine on trouve un groupe alcool secondaire et un autre nonsaturé CH:CH, situés dans deux noyaux hydrogénés différents, on a essayé d'établir la position du groupe alcoolique à l'égard de la double liaison.

Si on considère une des recherches de *Windaus*, et notamment que le cholestanon, la cétone de la cholestérine, a la formule :



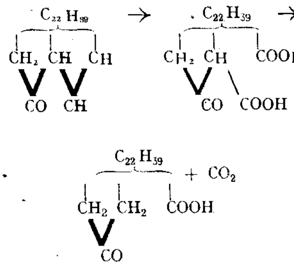
on constate que lorsqu'on le traite avec attention avec une solution aqueuse de permanganate de potassium afin de l'oxyder, le groupe *CO* reste intacte tandis que le groupe nonsaturé est attaqué. Au lieu de l'acide céto-di-carbonique :



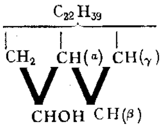
on obtient une scision du noyau et un acide céto-monocarbonique ($C_{26}H_{44}O_3$). [Ber. *39.* 2010 (1906); Ber., *50,* 133 (1917).]

L'acide céto-di-carbonique, $C_{27}H_{44}O_5$, qui parait se former au commencement, semble peu stable et met immédiatement en liberté du CO_2; il contient probablement un groupe carboxylique dans la position β en ce qui concerne le groupe cétonique.

La réaction est la suivante :



d'ou il s'ensuit que la double liaison occupe la position β; j-par rapport au groupe cétonique, et respectivement celui alcoolique :



Une fois étabie l'existence de ces deux noyaux comme étant voisins. *Windaus* [Ber. *39.* 2252 (1906); *37.* 2031 (1904)] a cherché à préciser le nombre des membres formant ces noyaux.

Il a réussi facilement à hydrogéner le noyau 2, de la double liaison et a le protéger de l'oxydation lorsqu'il scinde le noyau 1. Il a réussi également à protéger de l'oxydation le cycle 1, après avoir remplacé le groupe OH par H lorsqu'il scindait le cycle 2. Dans les deux cas on a obtenu des acides caractéristiques, di-carboniques, dans lesquels on a pu établir la position respective de chacun des deux groupes carboxyliques, en tirant plus tard la conclusion sur le nombre des membres de ces deux noyaux.

(To be continued.)

WATER TREATMENT.

An Interesting Exhibit at Wembley.

A most interesting example of the application of chemistry to industrial operations is in the treatment of drinking and general technical water supply, the science of which has made remarkable progress during the last few years. In this connection an interesting exhibit at Wembley is that of the Paterson Engineering Co., Ltd. (London), which, by invitation of the Ministry of Health, is housed in the Tropical Hygiene Section of the British Government Building, because a portion of the apparatus shown relates to sanitary engineering.

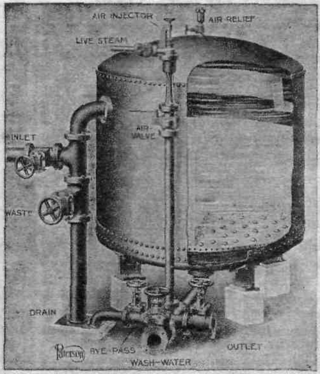


Fig. 1. Paterson pressure type filter.

The display consists of a model showing the latest type "rapid gravity" improved sand filter as installed at the Barn Elms Works of the Metropolitan Water Board, air-cleansed gravity and also pressure filters for the treatment of either drinking or industrial water, the "Chloronome" apparatus for the sterilisation of drinking water and the treatment of cooling water for steam engines and turbines so as to prevent organic growths in the condenser tubes, an electrolyser for the production of hypochlorite (an alternative method for sterilising drinking water) and a scale model of the patent by-pass "Osilameter" feed gear for large water softening plants, operating on the lime and soda ash principle.

The "Chloronome" is an ingenious apparatus for admitting continuously and automatically a trace of chlorine gas to water, and apart from sterilisation—particularly important in hot countries—the principle is valuable in preventing the formation of deposits of living organisms on the inside of the condenser tubes of steam engines and turbines. These form normally a slimy and tenacious deposit, which is a very efficient non-conductor of heat, especially as it also acts as a mud trap. The result is a rapid reduction in the heat transmission efficiency of the tubes and a lowering of the vacuum even in spite of ample volume of cooling water at a low temperature. The importance of this in the efficient operation of steam turbines does not need much emphasis since a drop of ¼in. in the vaccum corresponds to over 1 per cent. increase in the steam consumption.

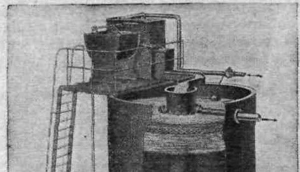


Fig. 2. Typical Paterson vertical sostening plant.

By the "Chloronome" process the amount of chlorine gas supplied from cylinders necessary to give this beneficial effect, essentially a semi-sterilisation, does not as a rule exceed one part per three million

parts of water, even in tropical countries or when the cooling water is contaminated by sewage, and there is the additional advantage of the saving in labour for cleaning the tubes and the shutting down of condensing plant. The same priciple is now being widely used for sterilising drinking water and it is stated that altogether 500,000,000 gallons of water per 24 hours is already being treated with chlorine gas and the "Chloronome" in this way.

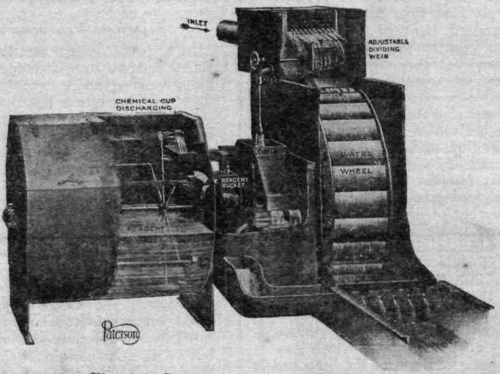


Fig. 3. Paterson Osilameter feeding gear.

An interesting section of the exhibit relates to the filtering of water. For large volumes, such as town supply, the "Paterson" rapid filter is supplied, as shown in the model, being a modern type of sand filter with periodical cleaning of the sand by compressed air agitation followed by a reversal of the water flow, of which single units or compartments with a capacity of 2,000,000 gallons each per 24 hours have been installed. In this improved design a bed of filtering sand is cleaned and ready for work again in a few minutes, whilst the speed of operation is about 50 times that of the old-fashioned sand filter, with equal efficiency and consequent sub-

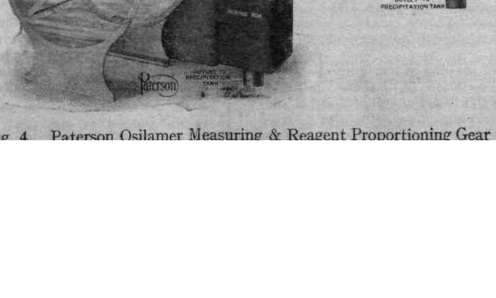


Fig. 4. Paterson Osilamer Measuring & Reagent Proportioning Gear

stantial saving in capital cost and floor space. For muddy water the "Paterson" gravity filter is used, which is combined, if necessary, with coagulation and sedimentation tubes, using for example sulphate of alumina, and another method available, depending on the conditions, is the "Paterson" pressure type filter, supplied usually in standard sizes of 50 to 5,000 gallons per hour, particularly interesting to the smaller user, but also employed, when necessitated by site conditions, for town water supplies.

The "Paterson" water softening plant, either of the horizontal or vertical type, operating on the lime and soda ash principle for the treatment of boiler feed-water is of course already familiar and the patent "Osilameter" feed gear for the re-agents possesses a number of distinctive features, the most characteristic of which is an adjustable weir which divides into two parts of any required ratio the flow of the unsoftened water into the plant. The large flow operates the agitating mechanism for keeping the lime cream constant motion in the storage tanks, and the minor portion is measured by a tipping bucket which controls the automatic addition of the lime and soda ash solution in exact proportions to the amount of water kowing without the use of valves, always liable to be stopped up by lime. The position of the dividing weir can be altered instantly by means of a hand wheel to give a greater or less dose of reagents, according to the varying quality of the water, whilst the container is of sufficient size to give ample supply for many hours, the whole forming a neat and extremely efficient arrangement which possesses the merits of simplicity and freedom from breakdown.

INSULIN.

[*Slightly abridged from the Report of the Lecture before the Royal Institution, March 28th, by Prof. HUGH MACLEAN, M.D., D.Sc.*

(*Continued from Page* 166.)

Standarisation of Insulin.

The effect of insulin in reducing the blood sugar is not confined to diabetic animals, for it reduces the blood sugar of normal animals as well. This effect of insulin is used in the standarisation of the product for clinical use, and the present unitage is based on the dose required to reduce the blood sugar of a normal rabbit to about 0.04 per cent. An average dose for a diabetic patient is 10 units, but the amount given depends on the gravity of the condition.

Symptoms Produced by Insulin.

In both the normal and the diabetic individual, insulin may produce definite symptoms when given in excess. The chief of these symptoms are hot flushes, especially on the face, weakness of the limbs, giddiness, sweating, tremulousness, and ultimately, if the condition is not relieved, convulsions, coma, and death. This property of insulin makes the remedy a very dangerous one unless great care is used in its administration, and no doubt explains many of the difficulties encountered by the earlier investigators.

The occurrence of these clinical phenomena is associated with the action of insulin in reducing the blood sugar. When the blood sugar gets too low, the fact is indicated by the appearance of these symptoms, but it is now certain that patients differ greatly as to the exact blood sugar concentration that may be present when the symptoms come on. Taking the normal resting sugar as about 0.1 per cent., it would seem that in certain subjects, even a slight decrease to about 0.08 per cent. or so may be associated with insulin symptoms, while, in others, the blood sugar concentration may be so low as 0.05 per cent., and yet the patient may feel quite well. In a general way, it is now established that the train of symptoms induced by insulin do not appear when the blood sugar is normal or above this level, but that they are liable to manifest themselves whenever the blood sinks to a sub-normal value; the exact level at which they appear depends on some unknown factors present in the patient. The association of these insulin symptoms with a more or less lowered blood sugar concentration—a hypoglycæmia—is, however, so pronounced that they are generally referred to as hypoglcæmic reactions. It may be taken for granted that when insulin symptoms do come on, the lower the blood sugar the more severe are the symptoms likely to be. Fortunately, these symptoms are very soon relieved if some glucose is taken, so that, generally, this insulin hypoglycæmic is not dangerous, provided that the patient

is warned as to the nature of the symptoms, and takes glucose immediately they come on. In certain circumstances, however, the condition may be a very real danger, as every one who has treated many patients must have found.

The *curious variation to the influence of* insulin which exists in normal individuals is well shown by the result of an experiment carried out in my laboratory on two young healthy medical men each about the same build, age, and weight. For a day or two before the test, both subjects took the same amount and the same kind of food. On the morning of the experiment each received 50 grams of glucose by mouth, and shortly afterwards 20 units of insulin were injected hypodermically. Samples of blood were then taken at frequent intervals for blood sugar estimations. One subject showed no symptoms whatever after the insulin, while the other developed symptoms so severe that it was difficult to get blood for sugar estimations. A further 50 grams of glucose given by mouth had a marked but only a temporary effect in relieving these symptoms, so that very soon the condition was as severe as before and indeed somewhat alarming. A further 60 grams of glucose were then administered, with the result that the insulin phenomena passed over *once again*, though some slight symptoms reappeared later. So far as blood sugar concentration was concerned, there was little difference between the subjects; in both the blood sugar fell to the region of 0.07 to 0.08 per cent. The description of his symptoms was as follows: " The first noticeable symptom was profuse sweating of the face, scalp and neck. This was very quickly followed by inability to perform fine movements with the hands, and weakness of the legs, which, however, was only noticed when standing up. General symptoms were dizziness, and an impression as of all near objects being far away and having a swaying movement. On recovery after glucose, the sweating, dizziness, and swaying were the first to go? the sense of weakness in the limbs remained for the longest time."

In the treatment of insulin hypoglycæmia, there is no difficulty in administering sugar provided the patient is still conscious; on the other hand, when the patient is unconscious, it may be very difficult indeed to get sugar into the system. In such cases the patient may generally be brought round by the injection of 1 c.c. of 1 in 1000 adrenalin solution. A dose of pituitrin (1 c.c.) given subcutaneously will also produce the desired result. If, however, consciousness is not soon restored by these methods, glucose must be injected into the circulation *through a vein. This procedure never fails* to bring the patient round, provided the hypoglycæmic condition has not last too long.

Though severe hypoglycæmic phenomena with unconsciousness were observed fairly often some time ago when our knowledge of the action of insulin was very limited, they are very seldom encountered at the present time, and should never ensue when the use of insulin is founded on a correct perception of its action and properties.

THE USE OF INSULIN IN DIABETES.

From what has already been said it is obvious that insulin does not cure diabetes. Insulin merely replaces a missing substance in the body of the diabetic, and so long as a *suitable dose of insulin is being administered*, the patient is free from symptoms and feels well both physically and mentally. When the administration of insulin is stopped the old symptoms reappear. In a typical case of diabetes the results produced by insulin are frequently dramatic. From being a weak, depressed, emaciated wreck, the diabetic very soon becomes a strong, energetic individual. The sugar and ketone bodies disappear from the urine, and there is nothing to indicate that the patient had ever been the subject of diabetes.

Suggestions have been brought forward in some quarters that the vigorous use of insulin may so rest the pancreas that a great improvement in tolerance may be established, and that in some cases a cure may be effected. In my opinion there is no basis for the expectation, and it is unlikely that insulin will do more in this direction that will a carefully regulated diet. There is a feeling among the public that once insulin is used *it must be administered* permanently, for it is believed that the condition of the patient who stops taking insulin is worse than if he had never begun it. This, however, is not so, for a patient may cease to take insulin and be no worse than he was before. Insulin is given by hypodermic injection, the average dose being from 10 to 20 units twice daily. It is usually injected about a quarter to half an hour before food,

and is given in the morning and at night, before breakfast and dinner respectively.

One of the most important points in the use of insulin is that the diet should be carefully correlated with the insulin doseage. As a rule, one unit of insulin will "look after" about two to three grams of carbohydrate, so that it becomes most important that an excessive amount of food should not be taken. It is just as necessary for the patient on insulin to follow definite rules as regards food, as it is for the diabetic patient who is being treated by diet alone. The only difference is that the insulin patient can take a more liberal diet. Once the diet is fixed, it must be adhered to, for a difference of diet would necessitate a difference in dosage of insulin, with the result that at one time the patient might be passing large amounts of sugar, while at another time the insulin might be in excess in relation to the diet, and the patient might suffer from the insulin symptoms already described. I have seen a patient who was taking a fairly large dose of insulin (20 units twice daily), but paying no attention to his diet, pass into diabetic coma.

(To be continued.)

GENERAL NOTES.

FIRST CONFERENCE OF SPECIAL LIBRARIES AND INFORMATION BUREAUX.

The *first Conference of Special Libraries* and Information Bureaux was held from 5th to 8th September, at High Leigh, Hoddeslon, Herts. Over 80 persons interested in the collection and dissemination of informative matter attended.

The objects of the Conference were outlined at the opening session by Dr. R. S. Hutton, Director of the Non-Ferrous Metals Research Association, and Mr. J. G. Pearce, Director of the Cast Iron Research Association. It has long been felt that many diverse agencies concerned with the treatment of information have problems in common, and needs an opportunity to establish mutual co-operation and assistance, and to determine their relationship to the press, and to the great municipal and national libraries and other institutions.

Subsequently, Mr. Allan Gomme, Librarian to H.M. Patent Office, London, Mr. B. M. Headicar, of the London School of Economics, and Dr. S. C. Bradford, of the Science Museum, South Kensington, addressed the Conference on their respective libraries.

Group meetings on the scientific, industrial and economic libraries were addressed by Mr. W. M. Corso, of the National Research Council, U.S.A., Miss L. Stubbs, B.A., and Mr. H. G. Lytall. The session on economic and statistical libraries indicated valuable developments which are taking place with regard to forecasting of trade tendencies.

An address by Lieut.-Col. J. M. Mitchell, O.B.E., Secretary to the Carnegie Trustees, outlined the policy of the Trustees with regard to Special Libraries, and Mr. L. Stanley Jast, Chief Librarian in Manchester, and Lieut.-Col. E. L. Johnson, Director of the Cleveland Technical Institution, dealt with Special Libraries in relation to other libraries and institutions.

Among the details of methods and equipment, Dr. J. C. Withers, of the British Cotton Industry Research Association, presented a paper on abstracting, and Mr. H. Rottenburg, of Cambridge, on a guide to scientific and technical literature. Bibliographical aids to Special Libraries, such as "The Subject Index to Periodicals" and "World List of Scientific Periodicals" were considered.

The important function of the press in collecting and distributing information was dealt with by Mr. F. H. Masters, Editor of "The Electrician," and Mr. B. C. Faulkner, Editor of "The Foundry Trades Journal," and at the concluding session, Dr. E. A. Baker, Director of the School of Librarianship, University College, considered the question of training men and women for work in Special Libraries.

The Conference, which was highly successful, provided abundant evidence of the interest in this field of work, and in order to ensure continuity of interest, without forming another Association, a Standing Committee of the Conference was appointed with power to consider matters in the interests of those engaged in directing or operating Special Libraries, and to convene a further Conference at some future date. This Committee is representative of a wide range of Institutions, and has already held its first meeting.

The most striking feature of the Conference was the keenness displayed by a large

number of highly diversified interests, including scientific, technical, industrial, wholesale and retail commerce, railways, political, agricultural, governmental, Universities, press, medical, sociological, and banking. This diversity served merely to emphasise the common interest of all these agencies in receiving, treating and distributing documetary material.

In this strenuous time when British Trade, in the face of such great difficulties both at Home and Abroad, is fighting to regain its pre-war position for exports to foreign markets and while Wembley is emphasising to the King's Subjects in particular and to the World in general the resources and possibilities of the Empire, it is opportune that an Italian, Signor Giuseppe Verzocchi, of Milan, has published a catalogue or, rather, work of art, proclaiming with splendid enthusiasm, the British product—"V. & D." Refractory Bricks—whose sale he controls and promotes in Italy with such marked success.

It is surely a happy augury of the days to which we confidently look forward when, once more, British goods will be everywhere demanded not only as being superior to all others but as being essential to the working out of successful business projects.

PROCEEDINGS AND NOTICES OF SOCIETIES.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

The next meeting of the Society will be held on Wednesday, October 1st, at the Chemical Society's Rooms, Burlington Piccadilly, W., at 8 p.m. The following papers wil be read:—

"The Determination of Coconut Oil and Butter Fat in Margarine," by G. D. Elsdon, B.Sc., F.I.C., and Percy Smith.

"A Preliminary Note on the Composition of the Fat of Goat's Butter," by F. Knowles, and J. C. Urquhart, B.Sc., A.I.C.

"The Quantitative Estimation of the Degree of Hydrolysis of Gallotannin by Tannase," by Miss W. N. Nicholson, B.Sc., and D. Rhind, B.Sc.

"The Pemberton-Neumann Method for the Estimation of Phosphorus," by Miss M. B. Richards, and W. Godden, B.Sc., A.R.C.S., F.I.C.

"Application of 'Formal Titration' to the Kjeldahl Method of Estimating Nitrogen," by W. S. Shaw, M.Sc., A.I.C.

Three candidates for admission to the Society will be balloted for.

THE INSTITUTE OF METALS.

The Third Autumn Lecture was delivered by D. W. M. CORSE, S.B. (of the National Research Council, Washington, D.C., U.S.A.) on Monday, 8th September, 1924, at 8 p.m. His subject was "*Recent Developments in Non-Ferrous Metallurgy in the United States, with Special Reference to Nickel and Aluminium-Bronze.*"

He described recent non-ferrous metallurgival developments in the United States with special reference to those that were new or those about which published information has been difficult to obtain.

The developments in the brasses and bronzes were so well covered by Sir Henry Fowler in the Second Autumn Lecture that no extended refernce to them was made.

Nickel was described from the historical standpoint and the various outstanding data in its developments were given.

The occurrence of nickel was discussed and the smelting of the ore into so called Bessemer described.

The refining methods differ with each of the three principal companies, although the smelting methods were practically the same.

Each method of refining was outlined, namely, the Orford, Mond, and Hybinette processes.

The properties of nickel were given and its commercial uses mentioned in detail.

The important alloy of nickel and copper called Monel metal was described, concluding with accounts of the Alloying Properties of Nickel and its Non-Metallic forms.

The copper aluminium alloy known as aluminium bronze was then described, with special reference to its commercial development rather than its scientific development.

This interesting series of alloys has found many important uses, such as for worm gear wheels for motor trucks, automobile parts and other structural pieces requiring resistance to vibratory stresses or fatigues.

The addition of lead to the standard aluminium bronze has given a new alloy of splendid wear resisting properties. The result of a special test of such an allow shows excellent results.

The dream of many a foundryman to avoid the use of sand for molding purposes may come true, if the new Holley "Long life mould" process using these moulds made of cast iron, proves to be the success that is at present indicated. This applies to mass production work. This process was described and results with reference to the economics and the practice were given.

The lecture concluded with short references to Ambrac metal, Frary metal, and the series of nickel chromium iron alloys occupying the field of metallurgy which may be called "No Man's Land."

Papers presented at the Annual Autumn Meeting, September 9th:—

"*A Method for Measuring Internal Stress in Brass Tubes,*" by ROBERT J. ANDERSON, B.S., and EVERETT G. FAHLMAN, B.S.

A new method was described for the quantitative estimation of longitudinal internal stress is tube shapes—for example, cold-drawn brass tubes. It was shown that the major stress is longitudinal, and the stress in the outer part of the wall of the tubing is a longitudinal compressive stress. The summation of the balanced stresses, of course, is zero. Absence of circumferential stress in tubes is indicated by the failure of diametrically cut rinks to spring in or out on being slit in two. Experiments showed that the usual cutting methods which have been applied to bars and rods for the estimation of stress are not applicable to tubes, especially where the hulk of the stress is longitudinal.

The method described in the paper for measuring longitudinal internal stress is called the strip method, and is carried out by slitting a narrow strip longitudinally in a piece of tubing; for example, a strip 2.75 inches long and 0.10 inch wide in a 3.25 inch tube length; and then releasing one end of such a slit strip by cutting. Stress is indicated by the springing out of the freed end and can be calculated by a formula based upon the modulus of elasticity of the material and the distance in movement of the freed end.

The method is useful for determining the amount of internal stress in cold-drawn effect of a low-temperature anneal upon stress release. It has often been thought that because cold-drawn brass does not crack on application of an accelerating cracking agent it is free from internal stress. The strip method is applicable for the quantitative estimation of stresses inferior to those necessary for cracking under the application of mecurous nitrate.

"*The Application of the Ideal Solubility Curve to the Interpretation of Equilibrium Diagrams in Metal Systems,*" by D. H. ANDREWS, Ph.D., and PROFESSOR JOHN JOHNSTON, D.Sc.

The applicability of certain deductions, from the laws of the ideal solution, to phase equilibria in metal systems, was indicated, and the practical usefulness of these theoretical relations in helping to assess and interpret the experimental data was shown. So far as the authors are aware, the method of plotting here discussed has not been applied to metal systems; indeed, some metallurgists appear to doubt the likelihood of any useful theoretical interpretation of these equilibrium curves. On the other hand, it is to be specifically understood that the simple mode of treatment outlined and illustrated in the paper may not, in the present state f our knowledge, be used without qualification as a basis for the complete interpretation of all types of system; nevertheless, in many systems the simple theory fits the observation better than the authors had anticipated, and so it may at least be used as a guide in criticising and simplifying experimental work.

"*Seventh Report to the Corrosion Research Committee of the Institute of Metals,*" by GUY D. BENGOUGH, D.Sc., and R. MAY, A.R.S.M.

The Seventh Report of the Corrosion Research Committee of the Institute of Metals considered the problem of corrosion largely from the point of view of the "Scale" of corrosion products which soon forms on the surfaces of such metals as copper, zinc and brass immersed in sea-water. In the Report an account is given of the more im-

portant reactions which lead to the production of these scales, and of the way in which they are affected by changes in the conditions surrounding the metal and in the composition of the metal itself. The studies of copper and zinc are preliminary to that of brass. An important feature of the Report is the study of the behaviour of high-speed streams of aerated sea-water in glass and brass tubes and the correlation of the behaviour of such streams with local corrosion. It is suggested that a large proportion of tube failures in modern condensers is due to local impingement of aerated sea-water, and that the actual distribution of corroded tubes in condensers often supports this view. The rapid corrosion is due to the local removal of protective scale by the impinging stream. Certain types of preformed scale however, may be very resistant to this type of action, and a useful field of work has been opened up in this direction. The occurrence of " dezincification " has been found to be due, not to bad mixing of copper and zinc in the maufacture of brass, but to the absence of arsenic from tubes; even a mere trace of arsenic has been found to prevent "dezincification" in condenser conditions. The presence of arsenic, however, is by no means always desirable and in some conditions a " dezincing " tube may behave better than a " non-dezincing " tube.

Careful observations on the electrolytic method of protection of condenser tubes have tended to throw grave doubts on the utility of this process, per se; usually the results are negative, but occasionally good results have been reported, and it seems probably that these must be due to chance secondary effects, particularly of the anode products; the great difficulty with which the process has to contend in condensers is the uniform distribution of the current along the tube; most of it is short circuited to the water-boxes, tube plates, etc., which are protected in preference to the tubes.

On the theoretical side the the view is adopted that the corrosion of brass may be due to metal-iron concentration cells or oxygen distribution cells; these may either reinforce or oppose one another according to the conditions. With high-speed water streams the metal-iron concentration cell maiy become the more powerful and render the metal anodic and severey corroded; deposits of sand, porous masses of corrosion products, etc., may cause oxygen distribution cells to become active and set up local corrosion, but the most rapid cases of corrosion seem to belong mainly to the former type. Sometimes the two types of action reinforce one another as when pits are started by oxygen-distribution effects, owing to the unequal porosity of the scale; the thin layer of scale which covers them is finally broken down by the action of an impinging aerated water-stream and the attack is carried on by the action of a metal-ion concentration cell.

The Report is a bulky document covering 150 pages, and contains a large amount of information about various and little known phases of condenser tube corrosion; it is impossible to give an adequate summary in the space at our disposal.

" *Comparative Results on Copper-Silicon-Aluminium and Other Aluminium Alloys as Obtained on Separately Cast Specimens and Specimens Cut From a Crankcase Casting*," by E. H. DIX, M.I.M.E., and LIEUT. A. J. LYON, B.S.

From the results of this investigation it has been concluded that the copper-silicon-aluminium-alloy is particularly well adapted for complicated castings which do not require a large amount of machining. In many parts used in the construction of aircraft engines, such as crankcases, manifolds, cover plates, and housing, require very little machining, and the finishing of the castings can practically all be done on a milling machine. This copper-silicon alloy is particularly well adapted for this type of work, and is recommended as a substitute for the No. 12 alloy wherever foundry difficulties due to shrinks, draws, and cracks offer serious difficulty. The casting properties of Alpax are very similar to those of the copper-silicon-aluminium alloy, but it is not considered a practical alloy from the Air Service standpoint, due to the fact that it has a very low proportinal limit and is inferior to the copper-silicon alloy in this respect. Lynite 195 is shown to have uniform and desirable physical properties. The proportional limit is considerahly above any of the alloys tested. The foundry practice, however, is more difficult for this type of an alloy, and the fact that it has to be heat-treated increases the cost of production. The tendency to warp and crack during the heat-treatment

would necessitate provision being made in the design for the use of this alloy; that is, a large complicated casting designed for either No. 12 or copper-silicon-aluminium alloy probably could not be poured in Lynite 195 with any degree of success. 8 per cent. copper-aluminium alloy is suitable for the general run of castings and can be cast in sections ⅛ in., or greater, in thickness without any great trouble. It is liable to shrinkage cracks, but this can largely be overcome in many designs.

"*The Determination of Sodium in Aluminium.*" by D. M. FAIRLIE, M.Sc., and G. B. BROOK, F.I.C.

A process was described in detail for separating sodium from aluminium which, while possessing reasonable accuracy, could be carried out by the average laboratory assistant. The difficulty of the process will be realised when it is stated that sodium has always appeared among the constituents specified by Government Departments as not allowable in aluminium beyond a trace (0.05 per cent., afterwards reduced to 0.03 per cent.).

The accuracy of the process is much greater than that yielded by the majority of analytical methods, particularly in view of the fact that the sodium is probably in suspension, and not in solution in the aluminium. With high purity samples of aluminium, showing a sodium content of 0.008 per cent., the result of many analyses show a mean error not exceeding 0.001.

"*The Extrusion of Brass Rod by the Inverted Process,*" by R. GENDERS, M.B.E., B.Met., F.I.C.

The experiments described in this paper and carried out on a manufacturing scale, although not extensive enough to constitute a complete study of the method of extrusion of brass rod by the inverted process, have provided ample data to show that the inverted process is incapable of producing internally defective rod when sound billets are used.

Precautions are necessary to secure good surface, the method adopted for the present being the avoidance of entrance of the skin of the billet into the region of flow. The increase in the proportion of discard so produced, although rendering the ejection of the billet shell more simple, brings the total discard above the ideal minimum of about 5 per cent., which might otherwise hav been possible. Even so, however, the pr portion is considerably less than in th ordinary method.

The observations of the relative pressure required by the two processes operated c a small scale are fully confirmed by th large-scale practice. For the same type of material, the pressure required by th new process is about 25 to 35 per cent. lower than for the ordinary process. Thi advantage must also be reflected in de creased wear and tear of the plant.

The structure of the extruded rod doe not show the concentric zones of materi varying in crystal size and physical proper ties often produced by the peculiar natur of the flow which obtains in the ordinar process. The rear portion of the rod i variable in structure and hardness fro centre to outside, but in a continuou gradient.

For the manufacture of ornamental sec tions and other types of material in whicl absolute reliability is not essential or is sub ordinate to the requirements of immaculat surface, the advantage of the inverte method lies mainly in its saving power For certain purposes it may be limited t some extent by the dimensions of th hollow plunger, although it is estimate that with a 1000 ton press, a container o 8¼ in. diameter and a plunger of 5½ in. bore can be used.

For the production of engineerin material, however, the inverted methoc possesses the advantage that all possibilit of the occurrence of the " core " defect i excluded, and that, if defects are allowed t arise, they will be visible on the surface of the rod. It is thus safe to extrude the billet nearly completely and so reduce scrap to a minimum without risk of the rod being affected internally.

The experiments carried out have beer confined to the production of 1-in. rod, bu no serious difficuty is foreseen in the appli cation of the method to the varied practice of the modern works.

Further work will be necessary before the method can be regarded as giving the best results of which it is capable. The experi ments described have, however, been suffi cient to confirm the previous small-scale work as regards the type of flow, interna soundness of rod, and the saving of power There seems to be no reason why extruded

rod made by this process should not rank as a thoroughly reliable engineering material.

"*The Effects of Impurities on Copper. Part II.—The Effect of Iron on Copper,*" by D. HANSON, D.Sc., and GRACE W. FORD, B.Sc.

Iron has been shown to exert a very considerable effect on the properties of pure copper; the effect of this impurity is, in many respects, very much greater than that of oxygen. The observed effects on the mechanical, electrical, and other properties are in keeping with the structure and constitution of iron-bearing copper, as revealed by a microscopical study of this material. Solid copper will dissolve about 4 per cent. of iron at 1100° C., but the solubility at lower temperatures is much less. Within the limits of solid solubility the effect of iron is considerable, particularly on the electrical resistivity, which increases rapidly as the iron content is raised: this increase is so rapid that iron must be regarded as extremely deleterious in copper for electrical purposes. When the iron content exceeds about 0.2 per cent., the effect on the resistivity depends largely in the heat-treatment of the material.

The effect on the tensile strength is less than might have been anticipated in the case of a soluble impurity, and, although in this respect iron has more effect than oxygen, it still produces a relatively soft material, even when the copper is saturated with iron. The tensile strength is raised by 2 per cent. of iron from 14.5 tons per sq. in. to about 20 tons per sq. in. The effect of heat-treatment is relatively small, in spite of the large differences in solubility of the iron, and a considerable improvement in strength as a result of heat-treatment, such as can be obtained in steel and some aluminium alloys, has now been realized.

Iron has no great embrittling effect, and copper containing iron can be rolled with great ease.

Iron is a deoxidiser for copper, but it creates difficulties during casting, owing to the formation of films that destroy the continuity of the metal. The deoxidising action is not great, as a considerable excess of iron would appear to be required to remove all the oxygen.

Copper containing iron as a sdle impurity is difficult to machine: it is soft, and "drags" under the tool.

"*The Relationship Between Tensile Strength, Temperature and Cold-Work in some Pure Metals and Single Solid Solutions,*" by DOUGLAS H. INGALL, M.Sc.

The tensile strengths of annealed and hardened wires of aluminium, silver, nickel, 70/30 Brass and 80/20 cupro-nickel at various temperatures were determined by the constant load and rising temperature method. In all cases a fundamental relationship is found with regard to tensile strength and temperature (previously shewn with copper) which is expressed by a straight line up to a critical inflection temperature and by a curved line for higher temperatures. The straight line portion of the curves may be expressed by the formula $Y = a - bX$ where Y = tensile strength, X = temperature and "a" and "b" are constants. A common relationship between the constants "a" and "b" and a common limiting value of X (critical inflection temperature) both expressed in terms of the melting point has been found for pure metals in the soft *annealed* state which would make the straight line portion of the curve fundamental in these cases. It is suggested that the critical inflection temperature is the all important property of any metal or alloy for high temperature service as it woud appear to be the temperature above which viscous flow may take place and below which there is only stability of the material in the cold worked state. Other things being equal, the higher the critical inflection temperature, the more suitable is the material and in this respect the experiments indicate that alloys of nickel, or any other metal of high melting point, which form a continuous series of solid solutions with a high temperature liquidus should prove to appear to the best advantage.

"*The Effect of Progressive Cold-Rolling on the Brinell Hardness of Copper,*" by H. MOORE, O.B.E., D.Sc., Ph.D.

In a paper recently published by Rawdon and Mutchler of the Bureau of Standards, U.S.A., it is stated that in the cold-rolling of copper, iron, tin and other metals and alloys, the Brinnell hardness rose rapidly during the initial stages of deformation and then diminished: "the metal becomes softer and in its final form may be softer than the metal in its initial stage." Experiments have been carried out at the Research Department, Woolwich, to test this sur-

prising conclusion. An annealed copper bar was cold-rolled from 3.12 inch to 0.0125 inch thickness, one half of the material being withdrawn for testing after each reduction of 50 per cent. of the thickness. The Brinell hardness number was 48 in the annealed bar, 98 after the first reduction of 50 %, rose at each subsequent reduction and eracbed 30 when the thickness was reduced to $\frac{1}{250}$ of the original thickness.

Balls of 5, 2, 1 and 0.8 mm. diameter were used in the Brinell hardness tests, care being taken in testing the thinner strips to avoid error arising from the use of too large a ball or load. The results give no support to the suggestion that severe cold-rolling of copper beyond a certain stage induces softening, and the author considers that convincing evidence of any such effect occurring generally in metals and alloy is still lacking.

" *Experiments on The Working of Nickel For Coinage*," by SIR THOMAS K. ROSE, D.Sc., A.R.S.M., and J. H. WATSON, M.C., B.Sc., A.R.S.M.

The experiments were made in order to determine the conditions in which nickel for coinage could be cold-rolled in the existing rolls at the Royal Mint.

It was fund impossible to prepare coins containing 99 per cent. nickel with 1 per cent. of manganese, magnesium, carbon, iron, silicon, etc., such as are manufactured with the aid of hot rolling. By the addition of 2 per cent. manganese however, castings can be prepared suitable for cold-rolling and conversion into coin. The carbon must not exceed 0.2 per cent. and the bars should be not less than 1 in. thick and 2 in. wide. The maximum crucible charge tried was 100 lb. Mond nickel with the addition of not more than 50 per cent. of scrap, makes a suitable charge. Four annealings are necessary, two at 800° during rolling and one at 675° after rolling and before cutting. The blanks are also annealed. Air is excluded during annealig. The blanks are cleaned before striking by rumbling in a wooden drum with half their weight of nickel pellets in a 2½ per cent. acetic acid solution for half an hour.

The coins consist of a solid solution and accordingly resist tarnishing and corrosion equally well with those containing 99 per cent. or more of nickel, such as are in circulation abroad. The two kinds of coin are indistinguishable in appearance, similarly magnetic and equally hard and resistant to abrasion. They appear to be similarly suitable for circulation.

Papers presented on Sept. 10th:

" *Some Experiments on the Effect of Casting Temperature and Heat-Treatment on the Physical Properties of a High-Tin Bronze*," by FRANCIS W. ROWE, B.Sc.

The author gave results of the effect of casting temperature and heat-treatment on a bronze of the following composition:—

Copper	86.0
Tin	15.95
Phosphores	.05

The alloy represented a bronze of the highest tin content which finds use in engineering practice and is used for special bearings where low tin phosphor bronzes and leaded phosphor bronzes have been found unsatisfactory.

Six boxes of test bars were moulded in greensand. Each box contained two bars 14 in. x 1½ in. diameter. The boxes were run at different temperatures. One bar from each box was machined into test bars and tested in the " as cast " state. One bar from boxes 1, 3 and 5 was annealed at 650° C. for 2 hours and one bar from boxes 2, 4 and 6 was quenched in water from 650° C. Tensile, hardness and impact tests were made on all bars. The impact test piece was not the usual B.E.S.A. standard but was 20 m.m. square with the standard notch 2 m.m. deep.

The larger size of bar was adopted to show differences in the bars in the " as cast " state.

The results of these tests are expressed in Table 1 and graphically in Figures 1 and 2 (Insert Figures 2 and 3).

The author also showed that although the greatest hardness (and probably the best wearing properties) was obtained with the lowest casting temperature. Such a casting temperature is, however, very often not practicable on account of the danger of " draws " in uneven sectioned castings.

" *Some Experiments on the Infuence of Casting Temperature and Mass on the Physical Properties of Admiralty Gun-*

Metal," by FRANCIS W. ROWE, B.Sc.

The author gave the results of some typical tests on admiralty gun-metal (copper 88 %, tin 10 %, zinc 2 %) conducted under works conditions.

Three boxes of test bars were moulded, each containing three bars, one 12 in. × ½ in. × ½ in., one 12 in. × 1 in. × 1 in., and one 12 in. × 2 in. × 2 in. The boxes were cast at 1200° C, 1150° C, and 1100° C. Tensile, hardness and impact tests were made on the bars thus btained. The 2 in. square bar was cut up to give a piece 7 ft. 8 in. square from the centre and two pieces ½ in. square from the outsides as in Figure 1 (Insert Figure 3). The ½ in. × 1 in. bars were machined straight into tensile and impact pieces. The result of the tests are expressed in Table 1 and graphically in Figures 2 and 3.

The figures showed the best results to be obtained in all sizes of bars with the lowest casting temperature, i.e., 1100° C., and the best tests of all with the ½ in. square bar cast at that temperature.

"*Studies in the Aluminium-Zinc System,*" by TOMOJIRO TANABE (Japan).

Previous investigations into the constitution of the alloys of aluminium and zinc have been very numerous, but work hitherto published has been almost entirely limited to thermal analysis and microscopic examination, and the results of tests in other directions, notably in the physical, are very few.

Accordingly, the present writer has investigated this system in various directions, to confirm the new diagram of Hanson and Gayler, and to make clear the nature of age-hardening.

The mechanical properties have also been studied.

"*Metal Spraying and Sprayed Metal.*" by T. HENRY TURNER, M.Sc., and W. E. BALLARD.

The Process of Metallisation invented shortly before the War and known generally as Schoop's metal spray process was considered. Held back in its development by the unsettled condition of industry, it is nevertheless being operated commercially at the present time in all the more important countries. The gas operated metal spraying pistol now used in this country is illustrated with a rumbling barrel type of metallising apparatus which is used for repetition work on small articles. Special devices side and inside of tubes and pipes. All articles to be sprayed are carefully sand-blasted, as it has been shown in practice that the metallic coatings adhere better to surfaces so prepared. In certain cases pre-heating of the article to be coated is recommended, as this again tends to improve the adhesion. By spraying lightly on to glass clips it has been possible to examine the individual particles of the sprayed metals. Photomicrographs of these show that the metal must be molten at the instant it strikes the surface to be coated. The remarkable shapes of the metal splashes shown will probably be of great interest to many. Solid articles have been built up by spraying and proved machineable and resonant.

Figures were given for the hardness and density of such built up metals. Tables were included which show the wire and gas consumption. Practically any metal available in wire form and fusible in the oxydydrogen flame may be sprayed on to practically any surface, e.g., on to paper, fabric, wood, or metal. The surface produced is always matte but may be polished if desired. The matte surface is an ideal foundation for paints. Considerable technical experience has now been obtained and completed structures are being uniformly coated all over with any desired metal for protection against atmospheric corrosion, chemical attack or furnace conditions. The process has also been used for building up repair and salvaging conditions. It has found a particular field in ship work and is recommended for the zincing of rail ends and fishplates for connecting purposes on electric railways as it does away with the necessity of copper connections and continual cleaning.

BOOKS RECEIVED.

A Reference List of Bibliographies, by JULIAN ARELL SETON and WILLIAM L. SCHAAF. Pp. X. + 100. New York: T. H. Wilson Co. 1924.

The Book of Receipts, by E. W. LUCAS, C.B.E., and H. B. STEVENS, O.B.E. Pp. 473. Twelfth Edition. London: J. & A. Churchill, 7, Great Marlborough Street, W. 1924. 10s. 6d. net.

ERRATUM.

The following concluding paragraph was inadvertently omitted from the review of IS IT GOOD ENGLISH? by JOHN O'LONDON which appeared in last

week's issue of The Chemical News, this vol., p. 169:

Lastly, writers other than scientific workers, frequently misuse the word "phenomenon." This is an instance in which the credit for correct usage must be given to scientists rather than to others.

One of the first prospectuses for 1924-5 to reach us is that from the Northampton Polytechnic Institute. The announcements give information concerning day and evening courses in Science and Engineering. The day courses commence on September 29, and the evening courses on September 22.

New Patents.

This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents' Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

20516—Austerweil, G.—Preparation of thymol from 2-cymidine. August 30.

20517—Austerweil, G.—Preparation of thymol from p-cymene. August 30.

Specifications Published This Week.

220413—Krafft, M.—Processes for the purification of burner gases and for obtaining chemically-pure sulphuric acid.

211167—Wacker Ges Fur Elektrochemische Industrie Ges, Dr. A.—Manufacture of acetic anhydride.

Abstract Published This Week.

218793—Synthetic resins.—Indurit. Products Co., Ltd., 4a, St. Andrew Square, Edinburgh, and Fairgrieve, J. G., Cherry Cottage, Uddington, Lanarkshire.

Articles of phenol-aldehyde condensation products are made by carrying out the condensation between a phenol and an aldehyde in the presence of cellulosic materials containing substantial amounts of oxycellulose and containing approximately 4 to 7.5 per cent. of lime and 0.5 to 1 per cent. of hypochlorite. A preferred material is that contained in the effluent waters of esparto paper mills, in which bleaching powder has been used. If the cellulosic material contains insufficient lime and hypochlorite, lime sludge is added thereto. In an example the suspended fibrous cellulose is separted from the effluent water, ground, mixed with phenol and formaldehyde and heated to about 50° C. The product is then ground and moulded under heat and pressure or moulded in the cold and afterwards heated under pressure. Wood pulp is also specified as a suitable cellulosic material.

Messrs. Rayner & Co. will obtain printed copies the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

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SESSION 1924-25.

COMMENCING ON TUESDAY, 7th OCTOBER, 1924.

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JOHN J. JACKSON, DIRECTOR OF EDUCATION, CITY HALL, CARDIFF.

THE CHEMICAL NEWS.

VOL. CXXIX. No. 3363.

September 26, 1924.

MERTON HOUSE, SALISBURY SQUARE,
LONDON, E.C.4.

TELEPHONES:
Administrative Central 6521
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ETUDE SUR LA CHOLESTERINE.

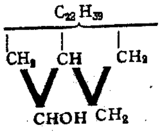
PAR PROFFESOR STEFAN MINOVICI, Ph.D. (BERLIN) F.C.S.

(*Continued from Page* 173).

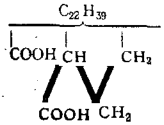
Pour établir la position des groupes carboxiliques; *Windaus* et *Dalmer* [Ber 52. 162 (1919)] ont appliqué la méthode Blanc qui consiste dans la manière dont se comportent les acides di-carboniques à l'égard de l'anhydride acétique.

Si on chauffe les acides di-carboniques 1.4 ou 1.5 entre 215-240° avec de l'anhydride acétique, on obtient leurs anhydres internes, tandis que les acides di-carboniques 1.6 ou 1.7, traités de la même manière, donnent naissance au penta ou hexacyclocétone, par example de l'acide pimélinique on obtient le cycli hexanon.

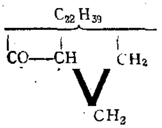
Quoiqu'on n'ait appliqué systématiquement la méthode de *Blanc* [Compt. rend. *144* 1356 (1907)] qu'a la série alifatique, on s'était cependant posé la question de savoir si la méthode ne pourrait également s'appliquer pour la série hydroaromatique, ce que Windaus a pu confirmer pour les combinaisons cycliques avec 5 et 6 membres. En diagnostiquant par cette méthode la cholestérine, il a réussi à la confirmer. Dans la recherche du cycle la il s'est servi de la dihidrocholestérine:



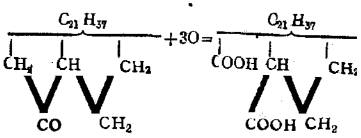
en l'oxidant par l'acide chromique, il a obtenu l'acide dicarbonique comme dérivé.



Par le chauffage de cet acide avec de l'anhydride acétique, on a obtenu la cétone, $C_{26}H_{44}O$ ou:



Cette cétone oxydée par l'acide nitrique se transforme en acide dicarbonique, $C_{26}H_{44}O_4$ dont la formation indique que dans la cétone ou trouve un groupe méthylénique.



Cet acide, $C_{26}H_{44}O_4$ traité avec l'anhydride acétique et par distilation dans le vide, donne un anhydride de cet acide et non plus une cétone, dont la formule est $C_{26}H_{42}O_3$, ce qui signifie que l'acide $C_{26}H_{44}O_4$ se comporte comme un acide dicarbonique 1.4 ou 1.5.

On peut déduire de ces considérations le nombre des membres du noyau 1. Car si

NOTICE OF REMOVAL.

On and after September 26 the Offices of the *Chemical News* will be at

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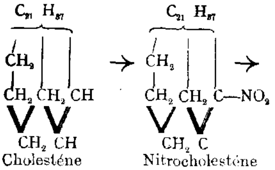
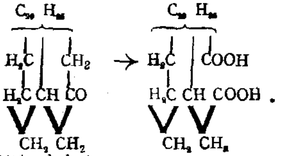
to which all communcations should be addressed.

la situation du groupe carboxyle dans l'acide $C_{27}H_{46}O_4$ et $C_{25}H_{44}O_4$ se différencie par une unité, il faut que l'acide $C_{26}H_{44}O_4$ possède les carboxyles dans la position 1.5 et l'acide $C_{27}H_{46}O_4$ dans la position 1.6.

En opérant de la même maniere sur le deuxième noyau [*Windaus*: Abderhalden. Handbuch der biologischen Arbertsmeth. Abt. I. Teil 6.], *mais en partant cette fois-ci* du cholestène, il est arrivé à conclure que par la scision du cycle, l'acide dicarbonique obtenu se comparte d'une autre manière à la distillation et qu'il ne donne plus une cétone mais une anhydride, $C_{26}H_{42}O_3$, qui peut passer très facilement dans l'acide respectif.



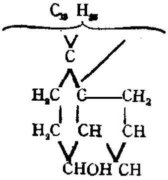
Cholesténe Nitrocholestène



Hétérochelestanon

Les carboxyles, par conséquent, doivent se trouver en 1.4 ou 1.5. Le cycle 2; doit contenir 4 ou 5 membres.

Les recherches feraient même croire qu'il en contient 5.



(Cholestérine)

Des quatre noyaux présumés, on ne connaît que la *position de deux d'entre eux*; en ce qui concerne les deux autres on n'a rien pu préciser jusqu'a présent.

En appliquant à la cholestérine une oxydation énergique, on a pu établir qu'il se trouve dans sa molécule aussi une chaîne linéaire assez longue. En vérité, en partant d'un *acide de la cholestérine*, le $C_{25}H_{42}O_6$, [*Windaus*: Ber. *45*. 1321 (1912); *42*. 3772 (1909); *41*. 2558 (1908); *46*. 1246 (1913)] on a pu obtenir avec l'acide chromique une décomposition en acétone et dans un acide tétra carbonique. $C_{22}H_{34}O_8$.

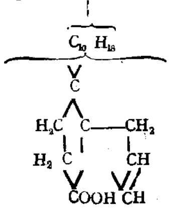
A d'autres oxydations plus fortes, on a *pu obtenir par scision une methylheptanone.*

On peut donner comme certain qu'il se trouve dans la cholestérine une chaine linéaire octilique :

$(CH_3)_2\ CH-CH_2-CH_2CH_2-CH-CH_3$

qui, à l'oxydation, donne le métil-isohexylcétone. [*Windaus* u. *Resau*: Ber. *46*. 1276 (1913).] De sorte que la formule de la cholestérine serait:

$(CH_3)_2CH-CH_2-CH_2-CH_2-CH-CH_3$



Le reste des autres dix atomes de C, doivent contenir encore deux noyaux saturés, l'un de leurs atomes se carbone faisant partie aussi des cycles 1 et 2.

Voici maintenant nos modestes contributions en ce qui concerne l'étude de la cholestérine.

On a constaté que la cholestérine, en présence de H_2SO_4 ou de HCl et dans un milieu alcoolique, donne naissance, par le condensation des deux molécules, à des éthers [Ber. *41*. 1562 (1908)] :

$$\begin{matrix} C_{27}H_{45} \\ C_{27}H_{45} \end{matrix} > O$$

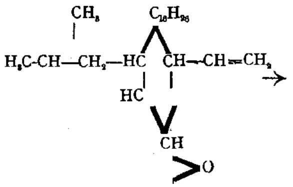
Nous nous sommes occupés ensuite de la

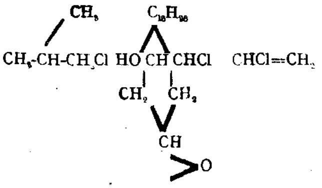
halogénation et de l'oxydation simultanée de la cholestérine [*Biochem. J.*, *38*, 46.].

Une ioduration a été impossible, les corps étant trop instables.

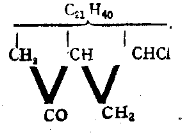
La chloruration et l'oxydation, indépendemment des méthodes courantes, été exectuées dans un milieu alcoolique, en nous servant du chlore gazeux. On a obtenu deux corps: l'un, le $C_{42}H_{72}Cl_2O_3$ et l'autre le $C_{56}H_{104}O_5Cl_2$.

Nous avons pu imaginer la constitution de ces corps en supposant que la cholestérine formait premièrement un éther oxyde qui, par halogénation et oxydation immédiate, perdait le groupe vinylique et isoamylique, en les remplaçant par du chlore et la groupe hydroxilique.



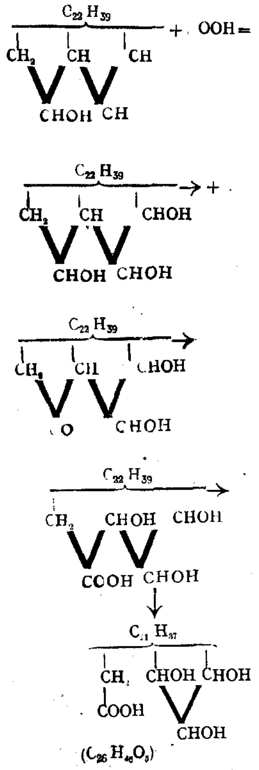


Nous avons également appliqué la chloruration et l'oxydation avec le perhydrol, en présence de HCl, obtenant un corps $C_{26}H_{47}ClO$, que nous croyons être une cétone chlorurée:



D'un autré côte nous avons entrepis l'oxydation de la cholestérine toujours au moyen du perhydrol en présence de l'H_2SO_4 concentré, obtenant [*Bull. Soc. Chem.*, ii 747 (1912)] un acide de la formule $C_{26}H_{46}O_5$.

Le " processus " peut s'expliquer ainsi: la molécule d'H_2O_2 s'additionne premièrement à la double liaison; deuxièmement, le groupe alcoolique du premier noyau s'oxyde en se transformant en cétone, et enfin a lieu l'oxydation du groupe cétonique en acide avec dégagement de CO_2.



Travaillant d'un utre côté toujours avec le perhydrol, H_2SO_4 dilué en milieu d'acide CH_3COOH glacial, [Bull. Sec. Sci. Acad. Roumanie *4*. 171 (1915)] nous avons *obtenu un corps indifferent aux caractères* d'une lactone, de la formule $C_{24}H_{40}O_4$ qui ne saurait être que l'acide précédent deshydraté et auquel on a oxydé deux groupes methyliques.

Dans cette même réaction nous avons obtenu aussi une résine acide qui ressemble à la colophane, ce qui nous donne un indice de plus que la cholestérine appartient au groupe des terpènes.

En ce qui concerne le rôle physiologique de la cholestérine, en dehors des diverses hypothèses données jusqu'a présent, dont notamment la propriété antihémolitique et anti-toxique, nous avons été conduits à considérer le rôle de la cholestérine dans l'organisme comme étant la trame sur laquelle doit s'étendre la structure de la matière nerveuse.

Nous basons cette hypothèse sur les considerations suivaites: la cholestérine est repandue dans tous les tissue de l'organisme mais c'est surtout dans le cerveau qu'elle se trouve en plus grande quantité, là où abonde la matière nerveuse. *Considérant* la résistance de ce corps, tant dans les réactions chimiques que dans les liquides de *l'organisme*, et d'un *autre côté le fait qu'on* l'a trouvée comme telle dans l'organisme, nous croyons que le rôle de ce corps ne peut être autre qúe celui de la charpente qui soutient la matière nerveuse, et quelles qu'auraient pu être les transformations de la matière nerveuse dans son exercice, la cholestérine reste intacte.

Nos recherches dans la direction des divers maladies, semblent confirmer cette hypothese.

Par ex.; dans la tuberculose on constate dans le cervau une diminuation accentruée des phosphatides (12 % au lieu de 18 %) et des acides grasses (6 % au lieu de 12 %), tandis que la cholestérine garde sa proportion (12 %).

En terminant, j'exprime milles remerciements pour votre bieuvellant attention.

Boulevard Carol 16,
Bucarest,
Roumanie.

THE PREPARATION OF ANILIDES AND ESTERS.

By Edward de Barry Barnett and Ivor Gray Nixon.

Anilides and esters are readily prepared in excellent yield by dissolving the acid (1 gram. mol.) and the phenol or primary amine (1 equivalent) in pyridine (2 to 3 parts), cooling in a freezing mixture and then slowly adding thionyl chloride (1 gram mol.) *After keeping for an hour at the* ordinary temperature the whole is poured into water and the precipitate washed with cold dilute hydrochloric acid and cold dilute sodium hydroxide. The method has been tested and found to give very good results with the following: *Acids.* Acetic, stearic, palmitic, benzoic, cinnamic, anisic, *o*-, *m*- and *p*-nitrobenzoic, 3:5-dinitrobenzoic anthracene-1-carboxylic. *Phenols.* Phenol, *o*- and *p*-nitrophenol, *p*-aminophenol, *o*-, *m*- and *p*-cresol, isoeugenol, catechol, resorcinol, quinol, 2-naphthol. *Amines.* Aniline, *o*-, *m*- and *p*-nitraniline, *p*-toluidine. Particularly good results were obtained in the *case of p-nitrobenzoic acid*, but very poor results with phenyl acetic acid. The method fails with diphenylamine and 1-aminoanthraquinone. It can be used for *the preparation of esters from some aliphatic alcohols*, but the results are uncertain. The following melting points given in the literature require correcting, the highest previously recorded figure being given in brackets: Isoeugenyl benzoate, 106° (103-104°). 2-Naphthyl-*p*-nitrobenzoate, 169° (166°). *o*-Nitrophenyl-*m*-nitro-benzoate, 129° (126°). *m*-Tolyl-*p*-nitrobenzoate 90° (85.5°). N-Phenyl-*p*-nitrobenzamide, 216° (204°). N-*p*-Nitrophenyl-*p*-nitrobenzamide, 274° (266°). N-*o*-Nitrophenyl-*p*-nitrobenzamide, 277° (220°).

The following new compounds were prepared and analysed, the calculated figures *being given in brackets:*

o-Nitrophenyl-*o*-nitrobenzoate; needles, m.p. 125°. C=53.9, H=2.54 (54.1, 2.78)

o-Nitrophenyl anisate; glistening needles, m.p. 96° C=61.5, H=4.30 (61.5, 4.26)

p-Nitrophenyl-*o*-nitrobenzoate; needles, m.p. 111°. C=54.3, H=2.54 (54.1, 2.78)

p-Nitrophenyl-*p*-nitrobenzoate; crystalline powder, m.p. 159° C=53.8, H=3.39 (54.1, 2.78)

p-Nitrophenyl-anisate; glistening needles, m.p. 166°. C=61.3, H=4.59 (61.5, 4.26)

p-Nitrophenyl-3:5-dinitrobenzoate; clus-

ters plus 1 mol. acetic acid, m.p. 188°. C=45.8, H=2.70, N=10.65 (45.8, 2.80, 10.68)

Catechyl-di-*p*-nitrobenzoate; woolly needles, m.p. 169°. C=58.5, H=3.20 (58.8, 2.94)

Quinyl-di-*p*-nitrobenzoate; microscopic needles, *m.p.* 258°. C=58.5, H=3.32 (58.8, 2.94)

2-Naphthyl-*o*-nitrobenzoate; clusters, m.p. 112°. C=69.4, H=4.03 (69.6, 3.76)

2-Naphthyl-*m*-nitrobenzoate; microscopic needles, m.p. 134°. C=69.5, H=4.01 (69.6, 3.76)

THE PREPARATION OF ACID ANHYDRIDES.

By Edward de Barry Barnett and James Wilfred Cook.

Acid anhydrides are frequently easily obtained by treating a solution or suspension of the acid (2 gram mols.) in ice cold pryridine (1 to 3 parts) with thionyl chloride (1 gram mol.) and then keeping at the ordinary temperature for about three hours. As a rule, the anhydrides are best isolated by pouring into ice cold dilute hydrochloric acid, and washing with cold very dilute sodium carbonate. If solid they are best recrystallised from a mixture of benzene and light petroleum. Anhydrides which react too easily with water to be isolated in the above manner can be obtained by direct fractional distillation of the reaction mixture, preferably under reduced pressure.

The yields obtained are usually about 70 per cent., but almost quantitative yields were obtained from *p*-toluic acid and anisic acid. The method fails with palmitie, stearic, phenyl acetic, *o*- and *p*-nitrobenzoic and 3:5-dinitrobenzoic acids.

INSULIN.

[Slightly abridged from the Report of the Lecture before the Royal Institution, March 28th, by Prof. HUGH MACLEAN, M.D., D.Sc.]

(Continued from Page 178.)

Some Difficulties Accompanying the Use of Insulin.

Naturally, the injection of insulin two or three times a day causes some physical discomfort, but when sharp fine needles are used this is not an important feature, and patients do not mind the slight pain of the injection. This reaction generally persists for about twenty-four hours, after which it gradually disappears. As more experience in the manufacture and purification of insulin is gained, these local reactions appear to be less and less frequently encountered, and at the present time no great amount of trouble is experienced on this account. Sometimes, especially during the early stages of insulin treatment, the legs begin to swell somewhat, but this soon disappears.

Continuous administration of insulin over long periods tends to produce a hardening of the skin around the site of injection, so that after some months a large area of the arm or leg may be markedly indurated. By varying the site of injection, and using different parts of the body, this difficulty may be largely overcome. It must be admitted, however, that the continuous administration of insulin to children is not always an easy problem, for the available surface for injection is not very large, and the skin of both arms and legs sometimes becomes so hard that it is difficult to insert the hypodermic needle. It is usually found that adult patients can inject themselves quite satisfactorily. On the whole, injection of insulin when carefully done does not give rise to so much difficulty as might perhaps be expected, but, on the other hand, there is no doubt that the advent of an effective preparation that could be given by mouth would be a very practical advance in diabetic therapy.

Diet in Insulin Therapy.

In order to obtain the best results from insulin, it is necessary to put the patient on a special diet containing but a small amount of carbohydrate, the rest of the diet being made up of protein and fat. The amount of food required by a diabetic patient varies according to many conditions, such as age, weight, and the amount of work done. It is now customary to express dietetic values, not by the weight of material consumed, but in terms of heat value or calories.

For practical purposes it may be accepted that 1 gram of protein or 1 gram of carbohydrate is equivalent to 4 calories, while 1 gram of fat is equivalent to 9 calories. Now a patient requires roughly a diet that will contain from 10 to 15 calories for each pound he weighs. Thus a patient weighing

140 pounds would require a diet containing from 1400 to 2000 calories, or he would probably do quite well on a diet containing about 1700 calories. In ordinary circumstances he would no doubt consume considerably more than this. It is essential that the diet should contain some protein, and 0.5 gram or somewhat less for each moderate amount, for it ensures safety in the use of insulin, especially during the earlier stages of treatment, and makes the diet more palatable.

PREVENTION OF INSULIN SYMPTOMS.

Since insulin symptoms do not come on until the blood sugar is reduced considerably below 0.1 per cent., it follows that no such symptoms are ever in evidence so long as the diabetic passes even a very small amount of sugar in his urine. Some medical men give just sufficient insulin to keep the urine almost but not entirely free from sugar, and thus guard against teh onset of any insulin symptoms. Where facilities for blood sugar estimations are available, it is best, however, to give sufficient insulin to reduce the blood sugar to about the normal level.

Though some failures in the use of insulin have been recorded, it is my experience that this remedy never fails to act in typical diabetes; whereas, if the patient is suffering from some other malady as well as diabetes, good results cannot always be expected.

THE FUTURE OF INSULIN THERAPY.

That insulin relieves the symptoms of diabetes there is no doubt whatever, but, unfortunately, its action is very liable to be interfered with by such causes as cold, an attack of influenza, a mild gastric upset, or almost any slight departure from normal health. The use of gas for removal of a tooth may cause a similar disturbance. In such cases, patients who were free from glycosuria and progressing satisfactorily may begin to pass large amounts of sugar in the urine, and may even suffer from marked diabetic symptoms. In these patients the dose of insulin must be very largely increased, but the correct dose may be difficult to determine. These interferences with the action of insulin render it necessary to keep patients treated with insulin under careful observation. Again, the fact that injection is necessary for the rest of the patient's life makes the use of insulin tedious and not altogether free from physical discomfort. It is difficult to contemplate children going on for forty to fifty years or more having two injections of insulin daily, and no doubt, in spite of insulin, many diabetic children will succumb to intermittent affections.

It is, of course, too early to say what the ultimate effects of insulin will be in the general treatment of diabetes. There is already a good deal of evidence pointing to the conclusion that some patients become, to some extent, accustomed to its action, so that larger and larger doses are necessary. The necessity for larger doses may only indicate a steady progression of the lesion, but a somewhat similar phenomenon is encountered in normal rabbits, which, when injected on several occasions with insulin, gradually show a markedly decreasd response to each administration. Recently some experimental evidence has been brought forward suggesting that, in normal circumstances, carbyhydrate metabolism may be somewhat different from what it is under artificial insuliu injection. Thus, when a dog is rendered diabetic by total removal of the pancreas, it is apparently impossible to prolong life *indefinitely* by the use of insulin, though, naturally, the dog can be kept alive by insulin for many months.

It might, therefore, be argued that there may be some cases of human diabetes comparable with the condition in the dog in which no active pancreatic tissue is present. In the ordinary diabetic subject there are, of course, some more or less active pancreatic islets left, and, further, there is no evidence that the production of pancreatic digestive fragments is at all interfered with. In the depancreatised dog no pancreatic digestive ferments are present, and so intestinal digestion is markedly upset. It has, therefore, been suggested that the inability to prolong the life of the depancreatised dog indefinitely by means of insulin depends on the absence of digestive ferments, and chiefly on the inability to hydrolyse fat.

While this is a possible explanation, it does not seem to be a very probable one, for it has been shown that the depancreatised dog may apparently be kept alive indefinitely, provided a *very small part* of the pancreas is left behind. If these experiments are substantiated, it is not likely that the absence of digestive ferments plays much part in the depancreatised animal, for the amount of digestive ferment secreted by a very small piece of pancreas would scarcely be sufficient to influence the fat

metabolism. Indeed, the evidence available at the present time points strongly to the probability that the pancreas forms another hormone essential for the process of normal carbohydrate metabolism beside insulin, and that unless the hormone is present, insulin alone will not sustain life for a long period.

Great as have been the results obtained by insulin therapy, it has not yet provided a substitute for the normal process from the clinical point of view, and much has yet to be achieved. On the other hand, the marvellous success of insulin in the treatment of severe and otherwise hopeless cases of diabetes is one of the most striking triumphs in the whole field of modern therapeutics.

EXHIBITS AT THE ROYAL PHOTOGRAPHIC SOCIETY.

A remarkable collection of photographs illustrating how the camera helps scientific investigations is shown at the 69th Annual Exhibition of the Royal Photographic Society of Great Britain, which now opens to the public at 35, Russell Square.

There are cloud photographs which have helped the meteorologist; a study in sand erosion, helpful to the geologist; a number of astronomical records, made to assist in the study of the skies, and many radiographs used by doctors or metallurgists to solve intricate problems.

Two groups of prints were actually made by wireless in New York. What happens when a revolver is fired is another pictorial record of great general interest. In the Survey and Record Section a panoramic view of the Sierra Nevada Mountains records scenery 135 miles away.

A taurid fireball passing near the star Polaris, photographed by Dr. William J. S. Lockyer, is considered to be probably the finest photograph of a meteor ever taken. The photograph shows nearly the whole path traversed by the meteor.

A Pictorial Photography section occupies the first floor gallery, and there are a zoological section and coloured photographical section in other galleries. There are also some fine portrain studies.

The exhibition will remain open daily except Sundays until October 25. Admission is free.

GENERAL NOTES:

INDUSTRIAL CHEMISTRY AWARD.

The Salters' Institute of Industrial Chemistry has made the following awards for 1924-25:—

Fellowships are renewed to Dr. W. G. Sedgwick, Armstrong College, Newcastle-on-Tyne, and Oxford, Fellow, 1923-24, and to Mr. W. Randerson, Imperial College of Science and Technology, Fellow, 1922-23, and hon. Fellow, 1923-24 (during tenure of Albert Kahn Travelling Fellowship). Fellowships are awarded to Mr. H. H. Evers, University of Liverpool; Mr. K. Knight Law, University College, Nottingham; Mr. H. S. Pink, University College, Nottingham, and Oxford; and Mr. V. E. Yarsley, Birmingham University. The Salters' Institute has also awarded 72 grants-in-aid to young men and women, employed in chemical works in and near London, to facilitate their further studies.

STAINLESS STEEL AS A COMMERCIAL PROPOSITION.

Miss C. Griff Charman, of the Women's Engineering Society, read a paper on "The Working of Stainless Steel" as a Conference of Engineering Societies at the Wembley Exhibition on September 16th.

She stated that as cutlery was for some considerable time the only use to which stainless steel was put the impression got about that it was too hard for any other purpose, but a lot of blame had been, and still was, put on stainless steel that should fall on the operator and bis tool. Stainless steel could he worked as a commercial proposition, but care and thought must be given to the quality and brand of the steel for each particular job, the method of handling, and the tools used, and overhead charges must be kept low to equalize the costs of material and labour.

of the Birmingham Association of Mechanical Engineers, in a paper on "Co-operation between the Engineer and the Works Chemist," said that the successful termination of the war was brought about by the development and application of scientific principles in both engineering works and on the battlefield, and there was no doubt that th war did, to a tremendous extent, make

the nation realize the value of science as never before. The future industrial prosperity and commercial supremacy of the Empire depended to a very large extent on the application of science to industry.

OPENING OF THE RAMSAY LABORATORY AT UNIVERSITY COLLEGE, UNIVERSITY OF LONDON.

His Royal Highness Prince Arthur of Connaught has graciously consented to undertake in November the formal opening of the Ramsay Laboratory of Chemical Engineering at University College, instituted in 1923 as part of the Memorial to the late Sir William Ramsay, K.C.B., F.R.S.

A full course of study in Chemical Engineering will be provided in the Laboratory in the coming session, leading to the Degree of M.Sc. or Ph.D. in Chemical Engineering.

The Course is designed to meet the demands of the manufacturing industries for men trained in the application of scientific methods to the design and operation of industrial chemical processes and plant. Special facilities are provided for research.

Full particulars can be obtained from the Secretary of University College, London.

THE STARCH IODINE REACTION.

By K. C. Sen, M.Sc.

The blue colouration obtained by adding iodine solution to a solution of starch has attracted much attention, though the constitution of this blue substance is by no means clear. Opinions are still divided as to whether this so-called "starch-iodide" is a true compound or an adsorption complex. Thus with the recent papers of Euler and Myrback (*Annalen*, 1922, CCCXXVIII., 1; *Arkiv. Kem. Min. Geol*, 1922, VIII., No. 9,[1]) the number of formulae assigned to the compound "starch iodide" has now reached thirteen, the iodine content varying from three to more than twenty per cent. As Barger and Field (*Jour. Chem. Soc.*, 1912, CI., 1394) have pointed out, this is in itself an argument against the hypothesis of a definite chemical compound. In contradistinction to this view of chemical compound formation Kuster (*Annalen*, 1891, CCLXXXIII., 364) has shown that the formation of the blue colour can be satisfactorily accounted for by adsorption. This view has been supported by Padoa and Savarè (*Atti. R. Accad. Lincei*, 1905, (v), *14*. I, 467), by Katayama (*Zeit. anorg. Chem.*, 1907, LVI., 209), by Berczeller (*Biochem. Zeit.*, 1917, LXXXIV., 106) and Bancroft has accepted the same view. (*Applied Colloid Chemistry*, 1921, p. 104). Very recently Lottermoser (*Zeit, angew. Chem.*, 1921, XXXIV., 427) from electric potential and other physical measurements has supported the same view. This also explains the observations of Rouvier (*Compt. rend.*, CXVII., 461) that different varieties of starch takes up iodine to a different extent, for it is well known that variation in the physical properties may greatly change the adsorption capacity of any substance.

In a previous paper, the condition of starch in solution and its adsorptive power over acids and bases has been examined. It is probable that pure starch forms neutral particles in water, and in migration of starch towards the anode under an electric force is probably due to adsorbed electrolytes in course of its preparation. This fact is important because the blue "starch iodide" which is also colloidal in nature, migrates towards the anode with appreciable velocity as compared to original starch particles. This behaviour suggests that in the formation of starch iodide, some ions are also adsorbed which give a negative charge to the starch particles. An examination of the literature shows that many investigators are of opinion that the blue starch iodide always contains some iodions or hydriodic acid with it. (Compare Mylius, *Ber.*, XX., 688; Roberts, *Amer. J. Sci.* (3), XLVII., 422; Lonnes, *Zeit. anal. Chem.*, XXXV., 409; and Hale, *Amer. Chem. J.*, 1902, XXVIII., 438). Chemical evidence also goes to show that the starch iodide behaves like an unstable iodide. By removing the iodine ions, the blue colour disappears. Thus oxidising agents like chlorine, bromine, nitric acid, chromic acid, iodic acid, acidified permanganate, dichromate, persulphate, etc., and silver nitrate, mercuric chloride etc. which remove I' ions, can destroy the blue colour. It is also well known that by the addition of soluble iodides in low concentration the blue colour is intensified. Thus I have found that the sensitivity of the starch iodine reaction is at least ten times more in presence of KI

than in its absence. Many other electrolytes, such as soluble bromides, calcium chloride, potassium chloride, zinc chloride, sodium, ammoniuh and barium chlorides, have been examined and it has been found that electrolytes which increase the solubility of iodine in water increases the blue colour of the starch iodide. The conclusion has been drawn from these experiments that the blue colour is probably due to the adsorption of complex iodions, notably tri-iodions but not due to molecular iodine. This view is supported by the recent experiments of Lottermoser (*Zeit. angew. Chem.*, 1924, XXXVII., 84) who has shown that the I_3' ion is most strongly adsorbed by starch, the adsorption curve being normal. The slight blue colouration which takes place when pure aqueous solution of iodine is added to starch solution may be due to the presence of iodions due to the hydrolysis of iodine in water. (Compare Bray, *J. Amer. Chem. Soc.*, 1910, XXXII., 932). It must be remembered also that starch is an easily oxidisable substance and a little iodine may be reduced giving the necessary iodions.

It has often been observed during estimations of iodine with starch as indicator, that just before the end point is reached, the blue colour disappears and instead a red colouration appears. The same sort of colour, but more intense, appears when excess of potassium iodide or bromide is added to a blue starch iodide solution. The colour seems to be of free iodine in solution. The experiments of Lottermoser (*loc. cit.*) throw some light on this point. He has shown that no noticeable adsorption of tri-iodions takes place in solutions of KI at concentrations greater than decinormal. Moreover, expulsion of free iodine from the surface generally increases with increasing concentration. Again in the first case the concentration of iodine is too small to give rose to the blue colouration. This may mean that the red substance is a mixture of starch and molecular iodine as has been obtained by Andrews and Goettsch (*J. Amer. Chem. Soc.*, 1902, XXIV., 865) from iodine and dry starch. Probably an analyogous case is that of adsorption of KI by silver iodide, where beyond a concentration of $M/_{300}$, the amount of adsorption decreases with the increasing concentration of the electrolyte (Lottermoser and Rothe, *Zeit. Phys. Chem.*, 1908, LXII., 359).

Recent measurements on the conductivity of starch iodide solutions have shown that by the addition of iodine solution to a solution of starch, a slight increase in the conductivity is observed. The increase in electric conductivity denotes that some ions are formed in the solution. This may be due to two factors. Firstly, a small amount of iodine may be reduced, giving some iodions in the solutions and secondly, by the adsorption of tri-iodions, some ions already adsorbed by starch may be forced out. Many such cases are known in the literature. Thus I have observed that in presence of barium, strontium and other adsorbable ions, the adsorption of copper ions by manganese dioxide is markedly decreased, and a previously adsorbed ion may be completely replaced by other less conducting ions when shaken with suitable solutions.

Many colloidal solutions show an appreciable conductivity, and a case is that of colloidal ferric hydroxide, which shows an increase of conductivity with the increase in the dispersed phase. This conductivity is almost entirely due to the micellar portion of the colloid for Duclaux (*Compt. rend.*, 1905, CXL., 1468-1470, 1544-1547; Kolloid Zeit., 1908, III., 126-134) has shown that by filtering the colloid through collodion under pressure, the filtrate shows no appreciable conductivity. It has been suggested by Dhar (*Jour. Phys. Chem.*, 1924, XXVIII., 125-130), that the conductivity of starch iodide is also due to the micellar portion of the sol, and this may be quite possible. It has been shown in a previous paper that ferric hydroxide when shaken with HCl, is stabilised by the preferential adsorption of H° ions and as such, some Cl' ions are bound to it, though no salt formation actually takes place. With starch probably a similar thing occurs, and the adsorption complex starch + I_3' determines the conductivity of the solution. This complex will also behave as an unstable iodide.

This constitution is further supported by a study of the effect of heat and light on a solution of starch iodide. When starch iodide solution is heated the blue colour disappears and only reappears on cooling. By heating for a longer period, the colour can be permanently destroyed. Bordier (*Compt. rend.* 1916, CLXIII., 205, 291) has shown that the blue colour can be destroyed by exposing the solution either to sunlight or to ultraviolet or X-rays. Thus the action of heat and light are the same in this case. Andrews and Goettsch (*loc. cit.*) advanced the idea that in the solution decolourised by heat, most of the iodine exists

as an organic iodide, but part of it is present as hydiodic acid. When the blue solution is heated for some time what happens probably is that the high temperature dissociates I_3' according to the equation $I_3' = I_2 + I'$. Some iodine is also reduced to HI and also the reaction $3I_2 + 3H_2O$ $5HI + HIO_3$ is accelerated. The net result is that the solution now mainly contains HI and HIO_3 and with the almost practical disappearance of molecular iodine, no I_3' formation can take place and hence no colouration results even when the solution is cold. It is well known also that traces of acids increase the rate of reaction between HI and HIO_3. It has been observed that when an acid is added to a solution of starch iodide decolourised by heat, the blue colour immediately reappears. Thus traces of sulphuric acid, nitric acid, hydrochloric acid, acetic acid, etc., will at once colour the solution blue. It is also significant that the iodine in the decolourised solution can be quantitatively estimated by adding an acid.

Another interesting fact in this connection is that traces of acid or KI makes the blue colour more resistant to heat. The presence of excess of iodine inhibits the destruction of the blue colour to a certain extent. This is evidently due to the tendency of these substances to shift the equilibrium from right to left in the equations given above.

My best thanks are to Prof. N. R. Dhar, for interest in this work.

Chemical Laboratory,
Allahabad University,
India.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE CHEMICAL SOCIETY OF JAPAN.

Papers communicated to the Society:—

Studies on the Absorption Spectra of Derivatives of Benzophenone, by TOMOKICHI TASAKI.

Preparation of Petroleum from Fatty Oils. Part III. Catalytic Decomposition of the Products of Dry Distillation of Calcium Oleate, by MASAKAZU INOUYE.

Chemical Investigation of Japanese Minerals Containing Rarer Elements. Part VI. Analyses of Zircon and Xenotime of Ishikawa, Iwaki Province, by KENJIRO KIMURA and TAKU UYEMURA.

THE INSTITUTION OF MINING ENGINEERS.

The Thirty-fifth Annual General Meeting of The Institution of Mining Engineers will be held in Conference Hall No. 2, British Empire Exhibition, Wembley, on Thursday and Friday, October 2nd and 3rd, 1924.

Besides the general business, Dr. Haldane will deliver his Presidential Address on "The Values for which the Institution Stands."

The following papers will be submitted for discussion:—

Salt Treatment for Miners' Fatigue, by SIR JOSIAH COURT, L.R.C.P., M.R.C.S. (Eleventh Report to the Committee on "The Control of Atmospheric Conditions in Hot and Deep Mines.")

The Food Requirements of Coal Miners, by PROF. K. NEVILLE MOSS, *M.Sc.*

The Mechanical Efficiency of the Human Body during work in High Temperatures: The Physiological Standardisation of the Kata-Thermometer," by PROF. K. NEVILLE MOSS, M.Sc. (Ninth Report to the Committee on "The Control of Atmospheric Conditions in Hot and Deep Mines.")

The Application of Gas Analysis to the Detection of Gobfires, by JOHN T. STORROW, and J. IVON GRAHAM, M.A., M.Sc. (Tenth Report to the Committee on "The Control of Atmospheric Conditions in Hot and Deep Mines.")

On Friday, October 3rd, 1924, the following papers will be submitted for discussion:-

Economics of the Coal-mining Industry, by EVAN WILLIAMS, President of the Mining Association of Great Britain. (Paper read before the Empire Mining and Metallurgical Congress, June, 1924, to be reprinted in the Transactions of the Institution.)

The Valuation of Mines and Minerals, and the Relation of Income Tax to Such Valuations, by R. L. A. DRON, B.Sc.

Note. The following papers, read before the Empire Mining and Metallurgical Congress, June, 1924, and reprinted in the *Transactions of the Institution* (August and September, 1924, Parts), will be submitted for further discussion:—

The Ventilation of Mines, by PROF. DOUGLAS HAY, B.Sc., and ROBERT CLIVE

(Trans. Inst. M.E., 1923-1924. Vol. LXVII, page 411).

The Rhymney Valley Compressed-air Installation, by EDMUND L. HANN (*ibid.*, page 442).

Problems of Mechanical Coal-mining, by SAM MAVOR (*ibid.*, page 456).

The Preparation of Coal for the Market, by F. S. SINNATT, M.B.E., M.Sc. (Tech.), F.I.C., and H. EUSTACE MITTON, M.Inst.C.E., F.S.I. (*ibid.*, page 481).

CHELSEA POLYTECHNIC.

A circular from the Chelsea Polytechnic announces Day and Evening Classes in Metallurgy.

The Laboratories are equipped for Wet and Dry Assaying, Metallography, Pyrometry and Heat Treatment.

The Courses are suitable for students desiring to become:—(*a*) Industrial or Analytical Metallurgists; (*b*) Candidates for University Degrees or the Institute of Chemistry Diploma in Metallurgy; and (*c*) Assayers, Chemists, Engineers, Foundrymen, etc.

SIR OLIVER LODGE ON WIRELESS.

In connexion with the Liverpool Week at the Wembley Exhibition, on September 22, Sir Oliver Lodge broadcast an address on "The Romance of Wireless."

In the course of his address, Sir Oliver Lodge said that the romance of wireless chiefly consisted in the fact that we were for the first time consciously using the ether of space as a vehicle for messages. We had long unconsciously used it—not when we spoke to each other, for then we only used the air—but when we smiled or winked, or nodded, or, on a larger scale, when we signalled by means of flags or semaphores, or when we flashed Morse signals by the heliograph. We were also employing the ether (though few people knew it) by ordinary telegraphy. The wire did not really convey the message, it only directed it to its destination. The power was transferred, not directly by the electrons, but by their electrostatic fields—that was, by the space intervening between them, a space which, like every other space, was full of ether, and which in a cable was limited to the annular channel between the metallic core of the cable and its outer sheath. If the voltage applied was too high, it was the insulator that was damaged, not the core; and if the insulator was punctured, the message was stopped.

DISCOVERY OF WIRELESS WAVES.

When a rapidly alternating source was used, however, true waves could be emitted into the space surrounding the wire. Portions of energy were broken off and shot forward by their own momentum, travelling with the velocity of light; not with the velocity of light in free space, but with the velocity appropriate to the insulating material—which might be about half the speed attainable in free space. The existence of these waves conveyed by wires was demonstrated, and their wave-lengths roughly measured, in experiments made by him at the top of Brownlow Hill, in Liverpool, in the University College, which was now the University of Liverpool, in 1887-88; and the theory of such waves was deduced from Clerk Maxwell's work. Just about the same time, that exceptionally great physicist, Heinrich Hertz—who died much too young—made the far more striking discovery that these waves could be generated and detected in free space, without any guiding wire at all. Electricity had momentum as well as elasticity; and those two requisites sufficed for the transmission of waves. Electric and magnetic effects occurred together; they were inevitably associated. The electric part gave the elasticity, or the recoil; the magnetic part gave the inertia, or the momentum. And combining the two, as Clerk Maxwell showed, we had all the prerequisites for the propagation of waves.

It was by this means that we saw: it was thus that we received light from the sun. In the sun the ether was set quivering by the vigorous oscillation of its electric charges. The waves travelled out in all directions into space; and a minute fraction of them was utilized to stimulate the sensitive receiving instrument located in our eyes. Thus the human race and animals had all along been utilizing the properties of the ether to convey information. The eye was our etherial receiving instrument; it was unconscious wireless telegraphy, an unconscious utilization of the ether.

MAKING THE ETHER "TALK."

But now we had taken a further step, not in any way more remarkable, but with more understanding of what we were doing, under conditions, therefore, which were more liable to attract our attention and stimulate our surprise. Instead of the eye as detector, we constructed artificial instruments, whereby we had to deal with much longer waves, though otherwise of precisely the same character as those with which the eye was competent to deal. We translated those signals into auditory vibrations, that was, vibrations of plates and of the air, and so made them accessible to the ear instead of to the eye. And we had constructed other ingenious artificial arrangements for producing and modifying those waves, in accordance with the vibrations of the human larynx. The sending and receiving stations were different from those that had arisen in the course of evolution; they were artificially constructed, and, accordingly, were better understood; but in essentials the process was the same. Waves were generated, and then modulated, in the ether; they travelled out in all directions; and some small fraction of them was utilized to stimulate the receiver and produce what we called a sound. We had in fact made the ether "talk," or, rather, transmit speech. Through the ether we could, as it were, speak round the world. It was certainly an amazing achievement; and all honour to those who had made it possible.

Humanity had attained a new instrument, a new weapon, a new mode of conveying thought, a new method of interconrse between the nations, almost annihilating space. Surely it would be a weapon of peace, surely it would promote better understanding. The commonwealth of nations, often called the British Empire, was peacefully disposed. They, with our cousins across the Atlantic, constituted the same race, speaking the same language; they were now welded together by this new method of communication. And if they only set their face to the right and determined to preserve the peace of the world, they would succeed. The ether welded the worlds together into a cosmic system of law and order. Let it weld all humanity together, so that they could face their common difficulties in a spirit of co-opetion and mutual trust!

SODIUM TUNGSTATES.

By EDGAR F. SMITH.

(Contribution from the John Harrison Laboratory of Chemistry—University of Pennsylvania.)

Having established the identity of the 4.10-salt, other considerations may claim attention (*J. Amer. Chem. Soc.*, 1922, XLIV, 2027). In many instances of preparation, the 4:10 and 5:12-salts are found together. To separate them by ractional recrystallization is not easy, but if a mixture of these salts be exposed to the air, the 4:10 salt gradually loses water, and is completely dehydrated in the course of a week or two. On covering such a dehydrated mass with water, heat is generated and the effloresced portion passes into solution, while hard, shining masses or crystals of the 5:12-salt remain.

The method is not absolute, but it separates these bodies to such an extent that resolution of each body and its recrystallization will give a pure product.

This experience led to the inquiry as to whether there was any probability of getting the 5:12-salt alone by the classic method of Scheibler, viz., the addition of hydrochloric acid to a boiling solution of the normal salt, until the alkalinity of the liquid had been in part neutralized (*J. prakt. Chem.*, 83, 278 (1861)). In a long series of experiments, which need not here be printed, the statement of the simple fact being sufficient, it was found that on adding hydrochloric acid to the boiling solution of normal sodium tungstate until the hydrogen ion concentration of the liquid lay between 10^{-6} and 10^{-7}, the first and second crystallizations gave analyses pointing clearly to the 5:12 salt. If, however the H-ion concentration was less than 10^{-7}, *e.g.*, between 10^{-7} and 10^{-8}, the first crop of crystals was a mixture (which analyzed for 9:22), and the filtrate from this mixture yielded a salt, the analysis of which again accorded very definitely with the theoretical requirements of the 5:12-salt. The acid used was a 20 % acid and was added in theoretical amounts. In one instance, where it was desired to prepare the 4:10-salt, the theoretical amount of acid was employed; it was slightly greater than that required in making the 5:12-salt, the H-ion concentration

being $10^{-6.2}$ to $10^{-6.8}$. The resulting crystals showed the ratio: 5:12.

On substituting acetic acid for hydrochloric acid, hoping to get the 4:10 salt, the product continued to analyze well for the ratio: 5:12.

These experiments indicate, therefore, that the hope must be abandoned of getting the 5:12, the 4:10 and the 3:7-salts by addition of the theoretically required acid.

There next arose the thought that the conductance curve of normal sodium tungstate (1:1), during its neutralization with hydrochloric acid, might offer a clue, in that break-points in the curve might appear which would bear some relation to the amount of acid required to produce the salts, in which the ratios of basic oxide to acid oxide were

5:12, 4:10, 3:7.

Accordingly, conductance curves were made, using weighed quantities of normal sodium tungstate and standardized hydrochloric acid. It soon became evident that temperatures, lying near the boiling point of water were requisite, and with the usual apparatus measurements curves resulted having one break-point, coinciding with the point where sufficient acid had been added to produce (theoretically) the salts which were sought, viz: the 5:12, 4:10, 3:7-salts.

The amounts of acid needed to produce these salts differ very slightly. Thus 32.36 grams of the normal salt, using an acid the strength of which is 0.1987 gr. per cc., will require

20.6 cc.	for the	3:7-salt
21.0 ,,	,, ,,	5:12-salt
21.6 ,,	,, ,,	4:10-salt

The acid requirement of the 3:7-salt proved to be closest to the break-point on the curve, and on that part of the curve where the conductivity began to increase; while the break-points of the 5:12-salt and the 4:10-salt cut the curve in very near succession to the 3:7-salt, along the slope of increased conductivity. Many additional experiments in this direction confirmed the preceding observation. Hundreds of analyses, also, of the well crystallized products were executed. It would only encumber the page to reproduce them here, while the outstanding fact is that, operating on normal sodium tungstate with hydrochloric acid, the product will be, and was, the 5:12 salt, where the H-ion concentration ranged from $10^{-3.6}$ to 10^{-9}.

(To be continued.)

NOTICES OF BOOKS.

Theory of Relativity: Studies and Contributions, by A. HENDERSON, A. W. HOBBS, and J. W. LASLEY, JR. Pp. IX. + 99. Mr. H. Milford, Oxford University Press, Amen House, Warwick Square, London, E.C.4. 11s. 6d. net.

Mathematical students have had ample opportunity of sharpening their wits when studying the various treatises on Relativity, and it may not be without interest to remark here that Relativity owes as much to mathematical science itself as to certain classical experiments involving the highest technical skill.

Take the case of the laws of physical systems being independent of the manner of measurement involving uniform rectilinear motion of the usual co-ordinate systems of reference. This is in general harmony with the application of the calculus to electrical or electromagnetic problems, where, by its aid, component variations are worked out quite independently of each other; in other words, a phenomenon may be analysed by considering it as a composite of independently superposed actions, each one obeying its law (or the law) quite independently of the others.

Relativity has profited directly or indirectly by this method; and it has drawn upon existing mathematical work of the highest order. The result has been a wider and remarkable method of analysis involving new concepts of *time* and *space*.

We have before us a book on Relativity which is the joint production of HENDERSON, HOBBS and LASLEY. This book of 99 pages is, so far as we are able to judge, exceedingly well composed. In terms of words, each page contains about 420, but in point of fact, many pages contain purely mathematical matter.

The purpose of the book is to present a clear and finished account of the Special and the General theory of Relativity. Reimannian manifolds, the quadratic differential form, and the theory of tensors are given; but the reader should have a preliminary knowledge of the theory of tensors.

It is claimed that a mathematician can follow the treatment without recourse to other works of reference. We venture to suggest that the non-mathematical student will find some pages of special interest, but he must understand elementary mathematics.

On page 16, in a foot-note, we observe that VOIGHT anticipated LORENTZ in respect *of the equations entering into the scheme of* LORENTZ Transformations, but no reference is given so that this citation may be looked up. The definite source may be familiar to some, but it cannot be familiar to all, as to-day so many are becoming interested in this new science.

Those wishing to follow the working out of illustrative relativity problems, involving the *special principle*, should turn to pages 22 to 24.

The section headed Theory of Tensors is particularly attractive and the introductory part, Gaussian co-ordinates, is very clear. The authors' style is above adverse criticism and the whole treatment is elegant and convincing.

We have pleasure in expressing our appreciation of the work, which is undoubtedly a first-class contribution to the subject, and the book should find a place in every scientific library.

The *printing*, or *letter-press* as it is generally termed, is perfect.

Complex Salts, by WILLIAM THOMAS, B.A., M.Sc. Pp. XI. + 122. London: Blackie & Son, Ltd., 50, Old Bailey, E.C.4. 1924. 10s. net.

It has only recently been possible to consider and discuss the nature and structure of complex salts. This has been brought about by the new theories and conceptions of the atom. These have indicated the ways in which inorganic complexes may be held together in stable combination. Previously it was customary to regard double salts as " molecular compounds " without any attempt being made to explain why they were capable of existence.

The author has based his method of treating the subject upon Werner's Co-ordination Theory. There is a brief reference to the earlier views on the nature of complex salts and allusion is made to the latest ideas and conceptions of valency. It should be realised, however, that these views must undergo modification and in some cases complete abandonment, since they do not always fit the facts.

The book does not cover too wide a range, and although much of importance in this field is not included, sufficient is given to stimulate interest in some of the difficult problems of modern inorganic chemistry. The chapter which is entitled " Resumé " is particularly useful from the student's point of view. The same may be said of the concluding chapter, in which the methods of preparation of a number of complex salts are described. These include potassium ferrocyanide and ferricyanide, sodium nitro-prusside and cobalti-nitrite and chloro-pentammine-cobaltic chloride.

This volume should take the place of those continental works on theoretical inorganic and general chemistry previously read by students preparing for final examinations.

Cadmium: It's Metallurgy, Properties and Uses, by NORMAN F. BUDGEN, PH.D. M.Sc. Pp. XIV + 239. London: Charles Griffin & Co., Ltd., Exeter Street, Strand, W.C.2. 1924. 21s.

Dr. Bugden's experimental work on cadmium is not unknown to readers of *The Chemical News*. His last contribution (Vol. CXXVIII., p. 232) indicated that the electrolytic method was the most accurate and expeditious one for the estimation of the metal in aluminium alloys.

In this volume, which is one of Griffin's *Series of Scientific Textbooks*, the author has made an exhaustive study of the chemistry and metallurgy of cadmium.

Owing to its high cost, cadmium has hitherto been neglected by metallurgists, but the time has now arrived when the supply and possible uses of all metals need to be examined carefully. Recently, cadmium has been tried with success as a substitute for (or an addition to) tin in the making of solders. The sulphide is also gradually being used in increasing quantities as a pigment, especially as " cadmium lithophone " in which it is admixed with barium sulphate. Other uses are cited by Dr. Bugden.

It is noteworthy that no ore rich in cadmium is worked directly for this metal, which is always obtained as a by-product in the working up of cadmiferous zinc ores, or more rarely, those of lead and copper. Diagrams are given on pages 8, 9 and 27 to show the stages involved in the extraction.

The chemistry of cadmium has been comparatively well investigated. Numerous salts are known and the properties of the element and its compounds have been studied in detail. Some idea of the extent of these researches will be obtained from the long lists of bibliographies which the author has appended to each of the eleven chapters. The history, sources, production, physical and chemical properties, estimation, alloys and uses of this uncommon element are all described very thoroughly.

This is, so far as the reviewer is aware, the first book on cadmium. In the writing and compiling it the author has accomplished his task in a commendable manner. Nothing of importance or interest in connection with the subject has been omitted. Technologists and metallurgists who have even but a remote interest in cadmium cannot afford to ignore this valuable contribution to the literature of applied science.

The Kinetic Theory of Gases, by PROF. EUGENE BLOCH. Translated by P. A. SMITH, B.A. (Oxon). Pp. XI. + 178. London: Methuen & Co., 36 Essex Street, W.C.2. 1924. 7s.

The kinetic theory of gases is the most highly developed section of the molecular theory of matter. It states that the continuity of solids, liquids or gases is only apparent, concealing a discontinuity beyond the limits of our perception. Matter in all its states is an agglomeration of minute particles, whose mutual interactions and movements depend on temperature and pressure, forming an assembly resembling a continuous medium.

In setting out the kinetic theory, it is perhaps natural that Prof. Bloch should give the work of French savants especially prominent mention. Thus emphasis is laid upon the undoubtedly important investigations of Perrin on the Brownian Movement; but it is stretching a point to term Boyle's Law, *Marriott's Law*, without reference to the discoverer except casually and in another connection in the preface.

On the whole, however, this account of the kinetic theory of gases is very good. The mathematical treatment has been most ably done, but the author assumes more than an elementary knowledge of pure mathematics far beyond the limits of many students. Advanced students, however, who are acquainted with higher mathematics, will derive much of value and interest from the book, which constitutes a valuable guide to the subject.

The first chapter entitled Distribution of Velocities: Laws of Perfect Gases, is very important, and with the second on real gases forms an introduction to the physico-chemical study of gases.

The utility of this translation is enhanced by the inclusion of a more complete bibliography than is contained by the original French edition which appeared in 1921.

Like its original, the book has no index beyond the new bibliography appended by the translator.

The Tutorial Chemistry Part II. Metals and Physical Chemistry, by G. H. BAILEY, D.Sc.Lond. Ph.D.Heidelberg. Edited by WILLIAM BRIGGS, L.S.D., M.A., B.Sc., F.R.S. Pp. VIII. + 511. Fifth Edition. London: University Tutorial Press Ltd., High Street, W.C. 1924. 7s. 6d.

This text-book contains an account of Physical Chemistry and of the Chemistry of the Metals, so far as they are required for Inter. and Final University examinations.

Considerable alterations were made in the fourth edition, and in the latest issue a number of new paragraphs have been added during the revision for the fifth edition.

The chapters on Radio-activity and Atomic Numbers are well written from the student's point of view.

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

21032—Compagnie de Bethune.—Production of ethyl sulphuric acid. September 5.

20998—Philipp, H.—Manufacture of colloidal sulpur. September 5.

21066—Synthetic Ammonia & Nitrates, Ltd.—Production of nitric acid from ammonia. September 6.

21067—Synthetic Ammonia & Nitrates, Ltd.—Process of producing ammonium nitrate. September 6.

Specifications Published This Week.

193851—Chemical Treatment Co.—Process of desulphurizing iron, steel, ferro-alloys, and copper, and a composition of matter for use in said process.

220668—Margulies, Dr. O.—Process for the production of new organic arsenic compounds.

220771—Badische Anilin & Soda Fabrik.—Catalytic production of hydrocyanic acid.

220807—Nelson, W. A.—Process for the production of ammonia.

Abstract Published this Week.

218694—Sulphuric acid.—Cowburn, A. W., Westinghouse Road, Trafford Park, Manchester.

In the manufacture of sulphuric acid, the heat produced in the sulphur burners is utilised to concentrate the acid. The hot gases from the burners may be passed over the acid placed in shallow pans in the flue leading to the Glover tower or the pans may be arranged in cascade form, and the hot gases passed through a sinuous flue directly beneath them.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

SHANGHAI MUNICIPAL COUNCIL.

ASSISTANT POWER STATION CHEMIST.

The Electricity Department of the Council requires the services of an ASSISTANT POWER STATION CHEMIST. The Council's Power Station contains about 121,000 kilowatts of plant. The duties of the appointment include the sampling and testing of coals both in the laboratory and, when necessary, in the Power Station, the testing of water, oils and stores and the carrying out of analytical investigations in connection with corrosion or other troubles which may arise in the system. The chemist will be responsible to the Power Station Chemist for keeping the various chemical indicating and recording instruments in the Power Station in order, supervising the keeping of records and obtaining the necessary technical information from such records.

Candidates should have had a sound education and taken a B.Sc. degree at one of the leading Universities. They should preferably have had practical experience in the chemistry of steam raising.

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The first engagement will be for three years. Free second-class passages out and home again and free medical attendance provided. Applicants must be unmarried.

Applications in writing only, giving full particulars as to age, education and training, to be sent on or before 6th October, 1924, to the undersigned, c/o Messrs. Preece, Cardew & Rider, 8, Queen Anne's Gate, S.W.1. Copies of not more than three recent testimonials and names of three references for personal character to be sent.

T. H. U. ALDRIDGE, M.I.E.E.,
M.I., Mech.E., Fel.A.I.E.E.
Engineer-in-Chief and Manager.

Dated 19th September, 1924.

THE CHEMICAL NEWS,

VOL. CXXIX. No. 3364.

MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

TELEPHONES:
Administrative Central 6521
Printing Works, Hop 2404.

THE ACTION OF HYDROGEN SULPHIDE ON A COOLED SOLUTION OF 1 PHENYL 5 METHYLBENZOTHIAZOLE 4′ DIAZONIUM CHLORIDE.

By F. RIXON and R. F. HUNTER, B.Sc., A.R.C.S., M.S.Chim., F.C.S.

During the series of investigations on dehydrothio p toluidine by one of us (R. F. Hunter, *Chem. News.* 1923, CXXVII, 385, 401, 1924, CXXVIII, 8, 18, 34, 54, 87, 103, 131, 260, 278, 414, and 1924, CXXIX, 37, 77) it was observed that when a stream of hydrogen sulphide is passed through a solution of the diazonium chloride of dehydrothiotoluidine that there is formed an orange red precipitate, resembling in appearance the precipitate obtained in the preparation of thiosalicylic acid by treating diazotised anthranilic acid with sulphuretted hydrogen at 0° C.

Since the amino group in the substituting phenyl group in 4′ Amino 1 phenyl 5 methyl benzothiazole has been shown (loc. cit.) to react normally with the usual reagents for the aromatic amino grouping, it is to be expected that when 1 phenyl 5 methyl benzothiazole 4′ diazonium chloride is treated with hydrogen sulphide, that the first product formed will be 1 phenyl 5 methyl benzothiazole 4′azo mercaptan (I) by the replacement of the chlorine atom of the diazonium chloride by a mercapto group, in the same way as the chlorine atom in the diazonium chloride of o aminobenzoic acid is replaced in the preparation of thiosalicylic acid

$$CH_3C_6H_3 \lessdot {}^{S}_{N} \gtrdot C\ C_6H_4N_2SH$$

(1)

NOTICE OF REMOVAL.

On and after September 26 the Offices of the *Chemical News* will be at

MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

to which all communcations should be addressed.

$$CH_3C_6H_3 \lessdot {}^{S}_{N} \gtrdot CC_6H_7SH$$

(2)

The compound (1) on warning should split off the azo nitrogen in the usual way to give the corresponding mercaptan: 4′ sulphydro 1 phenyl 5 methyl benzothiazole (2).

With regards the precipitate obtained in the first place by treating the diazonium chloride of dehydrothio-p-toluidine with sulphuretted hydrogen, this was filtered off, washed and placed aside to dry in a desiccator during the progress of other work. The substance was left in the desiccator for about a month, when it was found to have become a brown tarry material with which nothing could be done, the preparation was therefore repeated.

It will be recalled that when phenyl diazonium chloride is treated with phenyl mercaptan, that phenyl sulphide is formed, and hence, in view of this, it is to be expected that in the reaction between the diazonium chloride of dehydrothiotoluidine and hydrogen sulphide, that a certain portion of the mercaptan will condense with unchanged diazonium chloride with the production of a sulphide (3).

$$[CH_3C_6H_3 \lessdot {}^{S}_{N} \gtrdot CC_6H_4] : S$$

(3)

Actually it was found that the precipitate obtained as indicated consists of two substances which are conveniently separated by treatment of the product of the reaction with warm alcohol. On refluxing the product obtained from 1 phenyl 5 methyl benzothiazole 4′ diazonium chloride and

hydrogen sulphide with alcohol, partial solution takes place. On cooling the extract orange red crystals melting at 93° C are obtained which have a faint unpleasant mercaptan like odour. The brown residue which is insoluble in hot water has no definite melting point and appears to be the more complex substance (3). The compounds are present roughly in the ration of 1 to 4. The brown insoluble substance dissolves in glacial acetic acid and yields a precipitate of which is probably a brom addition product (R. F. Hunter, *Chem. News* 1924, CXXVIII, 147) on treatment with bromine in carbon tetrachloride. On continued boiling of the red substance extracted by alcohol with hot water a brown substance similar to the insoluble product in appearance and reactions is obtained.

EXPERIMENTAL.

4'Amino 1 phenyl 5 methyl benzothiazole

The laboratory preparation has already been described (R. F. Hunter, Trans. Soc. Chem. Ind. 1923, XLII, 302). In this case the substance was worked up from the dye intermediate purchased from the B.D.C., by extracting the latter with spirit, pouring the extract into water, collecting and drying the primuline-free compound and recrystallising from alcohol. Yellow crystals showing signs of softening at 170° and melting at 185° C were so obtained.

1 phenyl 5 methyl henpothiazole 4'diazonium chloride

4 gms of the above crystals were converted into the hydrochloride of the base by treating them with 40 ccs of 15 % hydrochloric acid, partial solution of the hydrochloric in hydrochloric acid took place, the suspension was cooled in a freezing mixture and diazotised with the usual precautions (R. F. Hunter, *Chem. News* 1924, CXXVIII, 131) using the theoretical amount of sodium nitrite in ice water.

ACTION OF HYDROGEN SULPHIDE.

The diazonium solution obtained above was poured into a large beaker kept in a freezing mixture of ice and salt, and was saturated with hydrogen sulphide for half-an-hour. An orange red precipitate was formed with much frothing due to the escape of gas from the precipitate. The beaker was removed at the end of half-an-hour and gently warmed over a wire gauze until the liquid boiled. Nitrogen and hydrogen sulphide being evolved and the precipitate coagulating to a single lump which was removed, washed and dried.

SEPARATION.

The dried substance was refluxed with 50 ccs of alcohol when partial solution took place. The brown residue was re-extracted with three other 50 cc portions of hot alcohol. The extracts united, filtered, concentrated and cooled, when orange crystals having a faint unpleasant odour, darkening at 85° and melting at 93° C were obtained.

YIELD 0.5 gm.

The substance gives a blood red solution with concentrated sulphuric acid and is soluble in nitric and hydrochloric acids, the nitric acid solution on pouring into water gives a yellow precipitate. Prolonged boiling with hot water gives a brown solid very similar in general properties to the insoluble material above.

The brown insoluble residue above, after drying, weighed 2 gms, softened about 120° and melted between 160° and 185°. The substance dissolves in hot acetone and hot glacial acetic acid. The solubility in hydrochloric acid and nitric acid is poor. The substance gives a blood red solution with concentrated sulphuric acid.

When bromine in carbon tetrachloride is added to a solution of the substance in glacial acetic acid there is formed an orange precipitate on standing of what is probably a brom addition product, (R. F. Hunter, *Chem. News* 1923, CXXVII, 385).

A portion of the substance was oxidised with sodium and hydrogen peroxides in a nickel crucible and gave barium sulphate corresponding to 18.2 % sulphur, that calculated for the sulphide (3) is 20 %. The experiments described in this paper can only be regarded as preliminary, but it is hoped to deal more thoroughly with the matter at a later date.

The Chemical Laboratory,
Highbury New Park, N.5.
November, 1923; and

The Chemical Laboratory,
The Regent St. Polytechnic, W.
April, 1924.

THE STRUCTURE OF ARSENIC.

By HAWKSWORTH COLLINS, B.A. (CAMB.).

By the application of the five main principles in the constitution of the elements that of As was obtained in *The Chemical News*, 1920, CXXI, 182 as CuC, i.e., NaCaC.

This deduction will now be proved to be true quite independently by means of the laws of relative volume and of heat of formation.

TABLE I.

The Relative Volumes of Arsenic.

As	=	Cu	+	C
12.98	=	9.54	+	3.44
As	=	Na +	Ca	+ C

	12.98	=	9.54	+ 0		+ 3.44
	15.68	=	0		+ 12.24	+ 3.44
aq.	18.94	=	0		+ 13.25	+ 5.69
	20.23	=	0		+ 14.54	+ 5.69
	19.58					
	11.38					

All the above volumes of Na, Cu, Ca and C have been demonstrated in previous papers. Also the volume of Na has frequently been shown to be zero; so the fact that three of the volumes of As split up into volumes of Ca and C with Na zero is not at all extraordinary.

The structural meaning of each of the two last volumes in Table I. is known, but cannot conveniently be given at present, because they are dependent upon certain other facts which must first be made evident.

TABLE II.

Experimental Data illustrating Table I.

	Relative Volume.	Theor. S.G. at 15° C.	Obs. S.G.
(224)	As 12.98	5.778	5.766 Mohs 5.884 Turner
(225)	As 15.68	4.78	4.71 Rettendorff 4.91 Spring
(226)	As 20.23	3.707	3.70 -3.71 15° Ruckoldt
(227)	As_2O_3 2(19.58) + 7.53 + 4.45 + 2.51	3.6906	3.690 Leonhard
(228)	As_2O_3 2(19.58) + 7.53 + 2(2.51)	3.83	3.85 Claudet
(229)	As_2O_5 2(19.58) + 7.53 + 4.45 + 3(2.51)	3.92	3.985 Playfair & J. 3.7342 Karsten
(230)	As_2O_5 2(19.58) + 7.53 + 4.51	4.054	4.023 Playfair & J.
(231)	AsI_3 19.58 + 3 (27.75)	4.434	4.39 13° Bodeker
(232)	As_2S_2 2(19.58) + 2(10.51)	3.5560	3.556 Mohs
(233)	As_2S_3 2(19.58) + 3(10.51)	3.480	3.48 Maidinger
	In the following six molecules 34.64 = 19.58 + 7.53 + 3(2.51)		
(234)	$Na_2HAsO_4 + 12H_2O$ 2(11.85) + 5.76 + 34.64 + 12(14.03)	1.73	1.736 Playfair & J.
(235)	$NaH_2AsO_4 + 2H_2O$ 2(11.85) + 2(5.76) + 34.64 + 2(14.03)	2,324	2.320 Dufet
(236)	KH_2AsO_4 22.29 + 2(5.76) + 34.64	2.63	2.638 Thomson
(237)	AmH_2AsO_4 23.87 + 2(5.76) + 34.64	2.27	2.249 Schiff 2.299 Schroder
(238)	$Cu_5(OH)_4(AsO_4)_2 + H_2O$ 5(9.54) + 4(2.51 + 5.76) + 2(34.64) + (14.03)	4.14	4.160 Dana
(239)	$Cu_5(OH)_4(AsO_4)_2 + 7H_2O$ 5(9.54) + 4(2.51 + 5.76) + 2(34.64) + 7(14.03)	3.17	3.162 Church 3.27 20°.5 Hillebrand
	In the following 5 cases 36.58 = 19.58 + 7.53 + 4.45 + 2(2.51)		
(240)	$H_3AsO_4 + \frac{1}{2}H_2O$ 3(5.76) + 36.58 + ½(14.03)	2.481	2.5 Nostrand
(241)	Na_3AsO_4 3(11.85) + 36.58	2.88	2.86 21° Stallo i.e., 2.87 15°
(242)	$Na_3AsO_4 + 12H_2O$ 3(11.85) + 36.58 + 12(14.03)	1.763	1.762 Schiff
(243)	$Na_2HAsO_4 + 7H_2O$ 2(11.85) + 5.76 + 36.58 + 7(14.03)	1.8995	1.8825 Dufet

(244)	$KNaHAsO_4 + 7H_2O$	22.29 + 11.85 + 5.76 + 36.58 + 7(14.03)	1.88	1.884 Schiff
(245)	Bi_3As_4	3(21.29) + 4(11.38)	8.47	8.45 Descamps
(246)	$SbAs_3$	21.29 + 3(11.38)	6.206	6.203 Rammelsberg
(247)	AgAs	10.1 + 11.38	8.47	8.51 Descamps
(248)	Ag_3As	3(10.1) + 11.38	9.5	9.51 Descamps.

In Nos. 227 and 228 the former has a volume 4.45 of oxygen, which becomes 2.51 in the latter. The same alteration of an oxygen atom occurs in Nos. 229 and 230. This change frequently takes place, and was demonstrated in the case of alcohols in the article on oxygen in *The Chemical News*, 1924, CXXVIII, 230.

TABLE III.

Heat of Formation of Arsenic.				Original Volume.		Rel. Vol. in combination at 15° C.		Change of Volume
solid	-35100	=	120 × (-3. 9) × 75	15.68	=	19.58	-	3.9
aq.	-29340	=	120 × (-3.26) × 75	15.68	=	18.94	-	3.26
aq.	-35100							

TABLE IV.

Experimental Data Illustrating Table III.

Heat of Formation.		Theor.	Obs.
(1) solid As_2O_3 - 2(35100) + 32341 + 2(96155)	=	154451	154670
corresponds with No. 228 Table III.			
(2) solid As_2O_5 - 2(35100) + 3(32341) + 2(96155)	=	219133	219380 T
(3) aq. As_2O_5 - 351000 - 29340 + + 3(32341) + 2(96155)	=	224893	225380
(4) solid $As_2 . O_5 . 3H_2O$ 219133 + 3(3205)	=	228748	226180
(5) aq. H_3AsO_4 - 3(15300) - 35100 + 32341 + 71515 + 2(96155)	=	215166	215230
(6) solid Na_3AsO_4 3(32706) - 35100 + 32341 + 71515 + 2(96155)	=	359184	360800
corresponds with No. 241 Table III.			
(7) aq. Na_2HAsO_4 (2(31234) - 24350 - 29340 + 32341 + 3(96155)	=	329584	329700
(8) aq. NaH_2AsO_4 31234 - 2(24350) -29340 + 32341 + 3(96155)	=	274000	273700
(9) aq. K_2HAsO_4 2(33000) - 15300 - 29340 + 32341 + 3(96155)	=	342166	339800
(10) aq. KH_2AsO_4 33000 - 24350 - 15300 - 29340 + 32341 + 3(96155)	=	284816	284000
(11) aq. K_3AsO_4 37274 + 2(33000) - 29340 + 32341 + 3(96155)	=	394740	396200
(12) aq. K_2I_2 2(37274) + 2(37720)	=	149988	150040
(13) aq. K_2O 2(33000) + 96155	=	162155	161800
			164560

The four oxygen atoms in Nos. 5 and 6 orrespond with those in Nos. 240 to 244 of able II.; whilst those in Nos. 7 to 11 correspond with Nos. 234 to 239.

The H.F. of the solid As_2O_5 does not orrespond with No. 230 in Table II. In rder that this may be the case, the H.F., stead of being 219133, would have to be 346761 = - 2(35100) + 32341 + 4(96155). It seems that Thomsen *calculated* his value, and not being aware of the fact that oxygen has three very different combining volumes and therefore three enormously different values of heat of formation, he brought into his calculations some previous determination which contained 2(32341) instead

of 2(96155). He made several similar miscalculations.

½ (a) If any one of the facts in Tables II. and IV. should be shown in the future to be wrong, the error would be confined to that particular experimental datum and to the corresponding theoretical deduction, and would not affect any others in the slightest.

(b) Again, Tables I. and III. contain secondary deductions upon the primary deductions in Tables II. and IV., and if any particular one of the former should be shown in the future to be wrong, the others would not be affected in the slightest; so that the deductions could not be demolished en masse, they could only be condemned to extinction one by one.

(c) In *The Chemical News*, 1924, CXXVIII., 161, the molecule Na_3AsO_4 was taken as an example to demonstrate the larger number of mathematical operations, which must be capable of successful performance upon each atom and also upon the molecule as a whole, in order that the experimental facts may be shown to fall in with the three laws of relative volume, heat of formation, and magnetic rotation.

From (a), (b) and (c) it must be evident that it is quite impossible for any one ever to upset this reasoning *in toto*, although one or two of the facts with their corresponding deductions may be demolished.

SODIUM TUNGSTATE.

By Edgar F. Smith.

(Contribution from the John Harrison Laboratory of Chemistry—University of Pennsylvania.)

(Continued from Page 199.)

These results have a suggestive value, but there constantly comes to mind the recollection that hydrolysis plays a very disturbing role with all soluble sodium tungstates.

While the literature enumerates about seventeen different sodium tungstates, only seven have been produced in aqueous solution, and the existence of two of these seven is in doubt. Formulating, then, these seven salts, for the sake of clarity, in a somewhat antiquated form, they arrange themselves thus—

I	II	III
$NaO . WO_3$	$Na_2O . 2 WO_3$	$3Na_2 . 7 WO_3$
1:1	1:2	1:2.33

IV	V
$5 Na_2O . 12 WO_3$	$4 Na_2O . 10 WO_3$
1:2.4	1:25

VI	VII
$Na_2O . 3 WO_3$	$Na_2O . 4 WO_3$
1:3	1.4

All are dydrated. The existence of I, IV, V and VII is not questioned. Number III was reported by Marignac. To some persons its existence has seemed problematical, yet evidence to be offered later confirms the statement of Marignac. As to the members II and VI, it is most regrettable that those who have sought to verify the statements of Lefort (Ann. chim. phys. [5] 9, 96 (1876)) have utterly failed. But why should these members not exist? Member VII is universally accepted. And, as its formula is contrasted with that of the normal salt (1:1), it seems to be only the latter ($Na_2O . WO_3$) to which have been added three molecules of WO_3—

$$Na_2O . WO_3 + 3 WO_3 \rightarrow Na_2O . 4 WO_3;$$

and indeed, the production of VII consists in introducing yellow tungstic acid into a boiling aqueous solution of member I, until no more of the added substance is dissolved, or until a portion of the solution removed to a suitable vessel and treated with hydrochloric acid does not give a precipitate of tungstic acid—in short, until the normal tungstic acid has been converted into the new meta tungstic acid—$H_2O . 4 WO_3$. This being true, ought not members II and VI be produced under analogous conditions? The following experiments deny this hope:

1. 50 grams of normal sodium tungstate were dissolved in 150 cc. of water. To the solution, heated on the water bath to 65° C., were added gradually thirty-five grams of WO_3, the calculated amount for the formation of the 1:2-salt. Upon concentrating the liquid, beautiful crystals separated, which analyzed closely the 5:12-salt.

II. Repeating experiment I, but using 100 grams of the normal salt (1:1) in 250 cc. of water, and adding 70 grams of WO_3, *in the cold*, the 5:12-salt was again produced.

It might be presumed that the above procedures would have and should have given the 1:2-salt, because calculated quantities of tungstic acid were added to definite

amounts of the normal salt to bring about this end.

III. In a third experiment 70 grams of WO_3 were gradually introduced into 200 cc. of water at 65° C., containing 50 grams of the normal salt (1:1). These conditions should have yielded the 1:3-salt, but the product was again 5:12.

Because the 5:12 sodium salt is an outstanding member in the series of soluble sodium tungstates, it may be well to recall that it has usually been designated "sodium para-tungstate" and is the starting-out substance from which chemists have regularly made other derivatives. In Laurent's arrangement of the tungstates (Ann. de chim. et de phys., *21*, 54) this salt received most consideration; to it he assigned the formula $5\ Na_2O\ .\ 12\ WO_3 + 28\ H_2O$. In this formulation Marignac concurred, but Scheibler, whose researches on the tungstates constitute a veritable classic, demurred and wrote the formula $3\ Na_2O\ .\ 7\ WO_3 + 16\ H_2O$, despite the fact that his analytical results, obtained from material of exceptional purity accorded best the requirements of Laurent's formula (Jr. f. prakt. Ch., *83*, 285). Hence, chemists were left in uncertainty, although Wolcott Gibbs (Ann. Chem. Jr., *1*, 223) and his contemporaries adopted the Laurent-Marignac view. However, in all these studies there was no conclusion as to the constitution of the 5:12-salt. Again, it was in the communication of Scheibler that hints on this point were found. He wrote (Jr. f. prakt Chem. *83*, 285):

> if the salt (para) be fused, on cooling it solidifies to an enamel-white, radiating crystalline mass, now partially soluble in water.

Two new salts, he declared, were formed. One of these was quite soluble in water. Its solution was very alkaline. The insoluble anhydrous salt he (J. f. prakt. Chem., *83*, 273 (1861)) assigned the formula $Na_2O\ .\ 3\ WO_3$, but in reality $(Na_2O\ .\ WO_3\ .\ 2H_2O)$, while to the insoluble product came the formula $Na_2O\ .\ 4WO_3$. In short, Scheibler got normal sodium tungstate and anhydrous meta-sodium tungstate by fusing sodium para-tungstate. He observed further that on heating the insoluble derivative with water in a stout glass tube to 120° C., solution of the material occurred. Upon evaporating the liquid pure sodium metatungstate (1:5) separated in beautiful octahedra. Also, on adding a large excess of glacial acetic acid to a concentrated aqueous solution of "sodium paratungstate" a syrup-like heavy layer, apparently wholly insoluble in the excess of acetic acid, settled on the bottom of the containing vessel. This syrup proved to be a concentrated solution of sodium metatungstate (1:4), but very impure; hence its identity was questioned. The writer, however, has been able to confirm these two observations of Scheizler again and again. Therefore, like the latter he too was impressed with the thought that "sodium para-tungstate" (5:12) is a double salt, having the rational formula

$$x\ Na_2O\ .\ WO_3 + y\ Na_2O\ .\ 4\ WO_3 + 28\ H_2O\ .$$

For the first time there is here presented a definite idea on the constitution of the 5:12-salt. But, strangely enough, Scheibler, in the face of the facts, felt that the pre-existence o the 1:4-salt in the 5:12-salt could only be assumed. The conviction of the writer, on the other hand, was and is that whenever tungstic acid is liberated from normal sodium tungstate by hydrochloric, acetic, formic, or any other acid, it —the tungstic acid, whether small or great in quantity—gives immediate rise to meta (1:4)-salt, and the latter instantly combines with an equivalent of the normal salt (1:1) to produce a double salt.

Nearly a quarter of a century passed before von Knorre (Jr. f. prakt. Chem., neue Folge (1883), *27*, 49) offered his views upon the formulation of sodium paratungstate—viz., whether it was $5Na_2O\ .\ 12\ WO_3\ .\ 28\ H_2O$, or $3\ Na_2O\ .\ 7\ WO_3\ .\ 16\ H_2O$. He melted the salt, then exhausted the fused mass with water, and analyzed the insoluble portion, which proved to be anhydrous 1:4, so that he was prone to think the 5:12 ratio was the correct ratio for the para-salts. He also dried portions of the 5:12 salt at 300°, a temperature at which the salt is fully dehydrated, but continues readily soluble in water. He had suspected the presence of sodium metatungstate in it. None was found. Hence it was inferred that the 5:12 salt was only resolved into its components by fusion. von Knorre next heated aqueous solutions of the 5:12-salt under pressure, but the results were not conclusive, although they indicated a production of normal salt (1:1) as well as the meta (1:4). While his experiments lacked finality, von Knorre argued that if the 5:12-salt consisted of the normal salt (1:1) and the meta (1:4), then on bringing them together in solution in the ratio of 5

parts of the 1:4-salt to 2 parts of the 1:1-salt, the 5:12-salt might possibly be regenerated. This proved to be the fact. There the study was permitted to rest for the time.

(To be Continued).

GENERAL NOTES:

COMMERCIAL—FINANCIAL—GENERAL.

ARTIFICIAL SILK.

The importance of applied science in Industry is shewn by the great business that has been established in the manufacture and sale of artificial silk, which is produced in many attractive colours. The leading company engaged in the business is Courtaulds, Ltd., which have numerous factories in Great Britain, and paid in dividends last year £1,800,000, and produces about 60 million pounds of the above commodity. The Company have a large capital and funds of about £8,000,000.

BRITISH GLUES AND CHEMICALS.

The report of the British Glues and Chemicals for the year ended May 31st announces that a basis of settlement of the company's taxation liability has now been arrived at with the Inland Revenue authorities; the exact figures have not yet been agreed, but provision is made in the accounts. After allowing for depreciation (£31,315) and bad debts, the net profit amounted to £6,293 (against £35,814 in the preceding year), to which is added the balance of £78,469 brought forward. Out of the total of £84,763, a sum of £76,000 is provided for the taxation liability to May 31st last, the balance of £8,763 being carried forward. The dividend on the 8 per cent. Cumulative Preference shares is in arrear as from October 1st, 1921.

ARSENIC IN BORAX.

At the Mansion House recently, before the Lord Mayor, the International Drug Company, of 16, Queen Victoria Street, pleaded "Guilty" on a summons alleging that they had sold purified borax adulterated with arsenic to the amount of 120 parts per million in excess of the five parts per million allowed by the British Pharmacopœia. Mr. W. N. Earle, solicitor, who prosecuted for the Corporation, said purified borax was used in lotions, ointments, and sometimes internally, and it was of the highest importance that it should not include more than the infinitesimal quantity of arsenic permitted by the British Pharmacopœia. He was not sugesting that any danger had arisen. Mr. Glyn-Jones, for the defence, said it was a case of commercial borax being supplied instead of the purified borax applied for. Borax was occasionally used as a mouth wash, but the amount in this instance was so negligibly microscopic that no harm could have arisen if a pound and a half had been consumed. All the adulterated borax had now been destroyed. The Lord Mayor fined the Company 40s., and ordered them to pay £2 2s. costs.

SAFETY IN MINES.

The Safety in Mines Research Board has issued a report dealing with the use in coal-mines of flame-proof electrical apparatus. The paper contains a report on the subject of flange protection which has been prepared by Dr. R. V. Wheeler in collaboration with Mr. I. C. F. Statham.

If an explosive mixture of firedamp and air is ignited inside the casing of electrical switchgear or other apparatus, *e.g.*, by an electric spark, the explosion causes an increase in pressure which, unless it be quickly released, may fracture or damage the casing; the casing must, however, be flame-proof, so that the flame of the internal explosion cannot set up an explosion cannot set up an explosion of fire-damp or coal dust in the atmosphere surrounding the apparatus. The problem of constructing casings safe for general use in gassy mines is one of reconciling these opposing requirements.

Several mehods have been suggested for affecting this; one of them, that of leaving a gap at the flanged joints of the casing sufficiently narrow to be flame-proof, yet sufficiently wide to give adequate release of pressure, is dealt with in the present report, which contains the results of a large num-

ber of experiments on the subject. The general conclusion drawn from these experiments is that, given careful attention to the design and mode of assembly of the casings "flame protection" can be relied upon; conclusions are also given as to the width and character of the gap and the breadth of the flanges in relation to the volume of the casing.

CANCER RESEARCH.

The Ministry of Health publishes an analysis of 20,000 cases of Cancer of the Breast, which is very illuminating on the ravages of this fell disease and the methods by which they can be combatted. Summarised, the following are the results:—

1. After performance of the older or "incomplete" operation, out of a net total of 7,029 patients, 2,956, or 29.2 per cent., were alive at the end of three years after operation.

2. After performance of the modern or "complete" operation, out of a net total of 8,921 patients, 3,857, or 43.2 per cent., were alive at the end of three years after operation.

3. With the "complete" operation the prognosis in intensively affected by the stage of the disease at which the patient is operated upon. Thus:—

(a) If the disease is still local and no secondary growth has occured, the percentage of survivors at three or more years after operation is from 65-80.

(b) If secondary growths have already occurred the percentage of survivors at three years after the operation falls to 30 or less.

(c) If the disease is very advanced some 8 to 9 per cent. only survive as long as three years after operation.

4. The expectation of life after the onset of cancer of the breast, where the disease runs its own course, may be taken as being on an average not more than three years and six months.

5. In the aggregate—*i.e.*, without reference to the stage of the disease at operation —the effect of "complete" operation is to prolong life, increasing the expectation of life from the onset of the disease by two to three years.

6. In patients operated upon by the "complete" operation, while the disease is still local, the expectation of life from the onset of the disease may be on the average as much as ten years more than in the case of persons not operated on.

MECHANICAL CLEANING OF BOILER FLUES.

An Interesting New Contrivance.

In spite of all the enormous developments in science and mechanical contrivances that have been perfected during the past century it is curious that steam boiler flues have always been cleaned out by hand. This is necessary about every six months in the case of the ordinary "Lancashire" boiler, for example, because of the accumulation of fine dust, especially when the fuel used is fairly high in ash. The job is an extremely unsatisfactory one, and even apart from the cost and troubles with labour, the principle of having to clean at long intervals results in a considerable loss of efficiency in the working of the boiler because the accumulation of the fine dust impedes the draught by reducing the effective area of the flues, and there is in addition, especially with a fairly high volatile fuel, the gradual formation of a deposit of soot and dirt on the boiler plates which constitutes an extremely effective non-conductor of heat, so that the combined effect is often very pronounced.

It is interesting to note, therefore, that a simple and ingenious apparatus known as the "Vulcan" mechanical soot cleaner, has been perfected by Messrs. The Boiler Tube and Flue Cleaner Co., Ltd., 238b, Grays Inn Road, London, W.C.1., by means of which the operation of cleaning boiler and economiser flues can now be carried out mechanically at short intervals, say once per day, thus keeping the flues and boiler plates and tubes in a permanently clean condition, with the elimination of hand labour altogether. This new cleaner consists essentially of a series of lengths of small bore steam pipe laid on at the bottom of the entire flue circuit from the furnace to the chimney, including of course the feed-water economisers, having steam nozzles is controlled by a patent manifold valve, placed say over the side flues in the case of a "Lancashire" boiler or in any other convenient position, which is operated generally once per shift. The design is such that the steam is turned on for a few seconds first to the nozzles in the boiler furnace tubes and bottom flue section, blowing in front of it all the light dust that has accumulated from the previous shift. Then, automatically, by the action of the manifold valve, the section of nozzles is shut out and the next comes into operation, and so on, in

this way the whole dust in the entire flue circuit being blown right out of the plant, either into a receptacle chamber at the end or up the chimney. The total time of operation is 2 minutes, and the amount of steam used is extremely small, whilst for the same reason there is no difficulty with damp flues, and the amount of material blown out of the chimney gives no trouble even in the case of inferior and high ash content fuels.

Further, the apparatus seems to be extremely simple and almost impossible to get out of order, whether by the heat or the fine dust, and does not require skilled labour. No cold air is admitted, and it is claimed that the annual inspection of a "Lancashire" boiler can be made 10 hours after pulling out the fires, whilst there is also a device of a drain cock normally open in the steam supply pipe, so that when not in operation no steam or water can leak into the flues.

It is gratifying to note that so much attention is now being given to the operation of the smaller boiler plants, which represent in the aggregate by far the largest amount of fuel burn, a fact that is rather apt to be forgotten.

GYPSUM.

The Dominion Bureau of Statistics issues the following finally revised statistics on the production of gypsum in Canada during 1923.

The total shipments of gypsum from Canadian deposits during 1923 amounted to 578,301 tons, valued at $2,243,100, as compared with 559,265 tons, worth $2,160,898, in the previous year. The production was made up of lump, crushed, fine ground and calcined gypsum sold; there was also included the calcined gypsum used in the calcining plants for the production of wall plaster, wall board, alabastine and other gypsum products. The average values, by grades, received by operators were as follows:—lump, $1.81; crushed, $1.90; fine ground, $6.14; and calcined, $11.28 per ton.

The output of gypsum rock totalled 558,853 tons, of which quantity 152,036 tons or 27 per cent. was calcined. Provincial quarry outputs were as follows:—Nova Scotia, 325,574 tons; New Brunswick, 81,549 tons; Ontario, 112,004 tons; Manitoba, 30,236 tons; and British Columbia, 490 tons.

MINERAL PRODUCTION OF CANADA DURING THE FIRST HALF OF 1924.

According to an official bulletin handed by the Dominion Bureau of Statistics at Ottawa to Reuter's Agency on September 6th, the metallic mineral production of Canada for the first half of the year shows an increase of 20 per cent. in value as compared with the same period last year. The *total value of the metallic productions* amounted to 47,498,000 dollars, as compared with 39,581,000 dollars last year. The gold production amounted to 14,415,000 dollars, being an increase of 3,511,000 dollars, and the silver production to 5,881,000 dollars, an increase of 374,000 dollars.

The value of the nickel produced was 10,216,000 dollars, an increase of 1,789,000 dollars.

The lead production amounted in value to 6,278,000 dollars, an increase of 2,700,000 dollars.

In the non-metallic section the coal production, owing to continued labour difficulties in Alberta, decreased in value by 10,584,000 dollars. The total metallic and non-metallic mineral production for the first half of the year is computed to amount in value to 84,341,000 dollars, as compared with 86,703,000 dollars for the first half of last year.

According to the Dominion Bureau of Statistics at Ottawa, the gold production of Canada from all sources during the calendar year 1923 amounted to 1,243,341 fine ounces, valued at $25,702,139, a decrease of 1.5 per cent. below the total for the previous year. The production for 1923 has only been exceeded in 1922 and 1900; in the latter year the Yukon placers reached the peak of their production and 1,350,057 ounces, valued at $27,908,153, was produced from lode and placer mines.

The prospectus of the Municipal College of Technology, Manchester, gives particulars of the University Courses for the Session 1924-25. A reduction in certain fees has been made for the coming session.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE BRITISH ASSOCIATION.

[*Toronto Meeting.*]

Presidential Address to Section M.—Agriculture, by Sir E. John Russell, F.R.S., entitled *Present-day Problems in Crop Production.*

The visits of the British Association to Canada have hitherto very appropriately coincided with definite stages in the progress of agricultural science and practice. It was at the Montreal Meeting of 1884 that Lawes and Gilbert presented their well-known paper on the sources of the fertility of Manitoba soils which ended the first great period of the development of agricultural science. This period had lasted eighty years; it had been ushered in with the precise and scientific work of de Saussure published in 1804; its outstanding features had been the foundation of agricultural science by Boussingault in 1834, its enrichment by Liebig's brilliant essay of 1840, and its systematic development by Lawes and Gilbert at Rothamsted from 1843 onwards. The whole purpose of the scientific workers of the period was to feed the plant; in Gilbert's own words the message of the crops on the Rothamsted plots was, "If you won't feed us we won't grow." The success of the new science was remarkable; its great triumph was the discovery of artificial fertilisers and their introduction into farming practice, and the workers had the great joy of seeing the crop yields rise considerably as the direct and recognised result of their labours. The problems were largely chemical, and agricultural science was regarded as simply a branch of chemistry. Gilbert's paper in 1884 was read before the Chemical Section, and it presented soil fertility as essentially chemical; a fertile soil, he argued, is one containing much plant food, especially nitrogen; it is one "which has accumulated within it the residue of ages of natural vegetation, and it becomes infertile as this residue is exhausted." At the time of the Toronto Meeting in 1896 a new period had begun, quietly and unnoticed, but growth was so rapid that at the Winnipeg Meeting in 1909 the subject had grown right away from chemistry; it had become a definite subsection, and its importance was so widely recognised that a recommendation was passed asking the Council to set it up as a full section, which was subsequently done.

In this second period the purpose was not to feed the crop but to study it; to discover what factors are concerned in the growth of crops and how they operate. This period, which may be called the period of free exploration, since the workers were not usually tied down to any particular technical probem, began almost simultaneously in the United States, in France, and in Germany. As soon as agricultural science was studied in the United States it became evident that the cultivation of the soil was at least as important as the feeding of the crop. This fact had of course been fully recognised in the English experiments, but the English farmer was so skilled in cultivation that he could be taught but little by science. The early American work as developed by Kedzie at Michigan, King at Wisconsin, Hilgard, and Whitney, was largely physical, and it greatly widened the outlook of agricultural investigators, opening the way to the extensive physical and physico-chemical studies which have now become so characteristic a feature of American work. The French investigators, particularly Schloesing, Muntz, Berthelot, and Déhérain, and the brilliant Russian, Winogradsky, then in Paris, revealed a new world of soil micro-organisms, the wonder and mystery of which appealed to the imagination of the younger workers in a way that none of the older utilitarian work had done. The Germans methodically explored the fields thus opened up; Hellriegel and Wollny accumulated a mass of data as to plant growth and soil changes which still remains of value to the student. These pioneers were succeeded by a host of followers whom it would be impossible to enumerate at length, and from whom it would be invidious to select a few. Moreover, the chemists and physicists of the old school were no longer left in sole possession; van Bemmelen introduced the conception of colloids, and at a later date Mitscherlich, Baule, and others developed the idea of mathematical expressions for the data of agricultural science. Sachs and his pupils in Germany, Déhérain, Maquenne and Demoussy in France, joined up the new science of plant physiology with agricultural science. The plant breeder also came in; Gregor Mendel's work, after lying hidden for forty years, was revealed to the world by Bateson and was at once turned

to agricultural use in England by one of Marshall Ward's pupils, R. H. Biffen; and in the United States by Webber and others. The selection method was developed to a high pitch of perfection in Canada by William Saunders, a revered leader in our science, whose dignified presence and kindly words of greeting remain as a vivid recollection of our visit fifteen years ago. His mantle has fallen on his son Charles, who has continued and developed the work.

The result of all this effort has been the accumulation of an enormous mass of information covering a very large part of the zeld with which agriculture has to deal. It has been essentially a pioneer period, with all the advantages of keen individual interest, controversy, sometimes even of excitement; but also with the disadvantages of a certain lack of perspective, failure to follow up important issues and some narrowness of outlook inevitable when a single individual is working alone at a great subject.

GENERALISATIONS THAT HAVE EMERGED.

But in spite of these drawbacks several important generalisations have emerged. One of the most pregnant in possibilities for the future is the recognition that the plant is a very plastic organisation and can be modified to a considerable extent within certain limits. Two methods are adopted: breeding, which may be on observational lines or on the Mendelian method of picking out the desired unit characters from plants in which they occur and assembling them in a new plant; and selection, in which a desirable plant is caused to produce seed from which stocks are multiplied. The scientific problems fall within the province of the science of genetics; the practical significance of the work lies in the fact that it greatly simplifies the agricultural problem by providing plants more or less suitable to the existing natural conditions where otherwise the expert would have the difficult, if not impossible, task of making the conditions suit the available plants. The work has proved extraordinarily fruitful and has given astonishing results even in our own time. It has played no small part in the amazing development of wheat growing in Canada. When the British Association went to Winnipeg in 1909 we were all impressed by the fact that Canada had then passed the 160-million bushel mark in production, but who would have thought that within fourteen years the production would exceed 474 million bushels? Even in England, where wheat has been grown for 2,000 years, and where farmers have a long traditional knowledge of the crop, the new varieties introduced by Biffen have increased the yields and the certainty of yields. The triumphs of Webber and others in the United States, of Nielson Ehle with cereals in Sweden, Jeffreys in standardising the quality of cotton in Egypt, the Howards in producing wheats for India, to mention only a few, are still fresh in our minds. In the first period in the development of agricultural science the honours in the matter of practical applications lay with the chemists for the artificial manures, but in the present period we must admit that they lie with the plant breeders and selectors who, indeed, are only on the threshold of what they may yet accomplish. And this great practical purpose of finding or producing varieties of crops specially suited to local conditions would be further advanced if the work were done in co-operation with plant physiologists who could precisely define the modifications required. Much saving of time and effort could be effected if it were possible to set up some International garden where small quantities of the plant breeders' productions could be grown, including those which each one has rejected as being unsuitable to his particular requirements. Many of these unwanted outcasts might prove of value in other conditions.

A second generalisation is that the soil is not a fixed, constant thing, but is pulsating with change. It contains a great population of micro-organisms which, among other activities, decompose the dead plant residues, producing nitrates, humic and other substances of great importance in crop production. But the numbers of these organisms fluctuate continually, and the bacteria at least change hourly; the nitrates suffer equally rapid changes in amount. Even the mineral part of the soil is not constant in composition. Modern research work shows that many of the properties determining fertility in soils are due to the soil colloids, and some of the most important are attributable to calcium complexes. These are unstable and are affected by the soil water. If the water is free from salts but contains carbon dioxide, the calcium may be replaced by hydrogen, and an acid soil results; if the water contains sodium chloride, the calcium is replaceable by sodium and the resulting complex may

is known, the changes are governed by the ordinary stoichiometric laws, the equilibrium following the usual course expected when a colloid is concerned. But the important fact emerges that any soil not well supplied with calcium contains within itself the possibility of becoming acid and therefore infertile, or alkaline and probably sterile, according to the nature of the soil water soaking through it. The various biological and chemical changes tend to alter the composition of the soil solution. Apparently, however, the colloids have a steadying or " buffering " effect, reducing the degree of acidity caused by the production of acids and absorbing or precipitating various ions that might otherwise cause disturbances.

A third important generalisation that has emerged is that the relations of the plant and the soil are not rigidly fixed but are capable of considerable variation, being profoundly influenced by a third factor, the climate. A soil moderately fertile in one set of conditions may be relatively unproductive in another. This happens repeatedly with soils containing much clay c much course sand. In Table I. are give the mechanical analyses of two soils, one c which, the Lias clay from England, is quit unworkable and remains derelict under ou conditions of cool temperature and moder ate but frequent rainfall, by reason of it high content of clay and fine silt; while th other, which contains even more clay, i capable of carrying good crops of grain an cotton under the hot dry conditions of th Sudan. The Western prairie soil is of simi lar physical type to that of the Englisl Weald soil, but while the prairie soil unde its climatic conditions of warm dry summe and cold dry winter is, and is likely to re main, a fertile wheat producer, the Weal soil under the wetter conditions of Englan is less fertile. In hot dry conditions th clay is no disadvantage and may even b an advantage, but in wet conditions it be comes a serious drawback; indeed, it migh be possible to find some mathematical re lationship between rainfall and degree c objectionableness in clay.

TABLE I.

Soils of similar type as regards mechanical analysis, but varying greatly in fertility by reason of climatic differences.

	Rich in finer fractions				Rich in coarser fractions	
	Waste land very difficult of cultivation	Fertile soil, millet & cotton	Poor farm land difficult to cultivate	Good prairie soil, Wheat	Waste land, Norfolk	Market garden, Anglesey
	Lias clay Oxfordshire	Sudan	Weald clay, Kent	Brandon	22 in. rain	35 in. rain
Coarse sand, 2.0 to 0.2 mm.	0.7	7.6*	1.5	2.5	62.4	93.7
Fine sand, 0.2 to 0.004 mm.	2.0	20.9	11.0	15.4	25.7	2.8
Silt, 0.04 to 0.01 mm.	6.4	12.6	19.6	17.7	0.2	0.5
Fine silt, 0.01 to 0.002 mm.	22.0	12.6	26.8	16.1	1.8	0.4
Clay (below 0.002 mm.) ...	41.0	55.9	22.1	29.2	0.6	Nil

*Mainly black nodules of calcium carbonate.

It appears then that if a fertile soil were carried from one country to another its productive power would not necessarily be carried with it. Its fertility is, to a considerable extent, dependent on the fact that it fits i with the climatic factors in producing con ditions favourable to good growth (desirable crops.

COMPLEXITY OF THE PROBLEM: METHODS OF ATTACK.

The agricultural investigator is thus confronted with three closely interlocking agencies—the plant, the climate, and the soil—each of which is variable within certain limits, and each playing a large part in the crop production which it is his business to study.

Confronted with a problem of this degree of complexity there are two methods of procedure: the empirical method of field observations and experiments, in which there is no pretence of great refinement and no expectation that the same result will ever be obtained twice, it being sufficient if over an average of numerous trials a result is obtained more often than would be expected from the laws of chance; and the scientific method, in which the factors are carefully analysed and their effects studied quantitatively; a synthesis is then attempted, and efforts are made to reconstruct the whole chain of processes and results. The scientific method is, of course, the one to which we are naturally attracted. But common truthfulness compels one to admit that up to the present the greatest advances in the actual production of crops have been effected by the empirical method, and not infrequently by men who are really artists rather than men of science, in that they are guided by some intuitive process which they cannot explain, and that they have the vision of the result before they obtain it, which the scientific man commonly has not.

The best hope for the future lies in the combination of the empirical and the scientific methods. This is steadily being accomplished by the recent strong infusion of science into the art of field experimentation, which has much enhanced the value of the field work and the trustworthiness of its results. Modern methods of replication, such as have been worked out at Rothamsted, and in the United States by Harris of the Carnegie Trust (Cold Spring Harbor), Kiesselbach in Nebraska, Myers and Love of Cornell, and others, constitutes a marked improvement in plot technique. And the figures themselves, besides being more accurate, can be made to yield more information than was formerly the case.

Great advances have been made in the methods of analysing the results. The figures are never the same in any two seasons, since the climatic conditions profoundly affect the yields. A few men, like J. H. Gilbert, have the faculty of extracting a great deal of information from a vast table of figures, but in the main even the trained scientific worker can made very little of them. The reason is that he has been brought up to deal with cases where only one factor is varying, while the growth of plants involves the interaction of three variable factors: the plant, the soil, and the climate. It is impossible to apply in the field the ordinary methods of the scientific investigator where single factors alone are studied; very different methods are needed, adapted to the case where several factors vary simultaneously.

Fortunately for agricultural science, statisicians have in recent years worked out methods of this kind, and these are being modified and developed by R. A. Fisher and Miss Mackenzie for application to the Rothamsted field data. It so happens that this material is very suitable for the purpose, since a large number of the field experiments have been repeated every year for seventy or eighty years on the same crop and on the same piece of land, using the same methods; the field workers also remain the same for many years, the changes being rare and without break in continuity. Although the statistical investigation is only recently begun, mathematical expression has already been given to the relationship between rainfall and yield of wheat and barley under different fertiliser treatments, and precision has been given to some of the ideas that have hitherto been only general impressions. If on an average of years a farmer is liable to a certain distribution of rainfall, it is becoming possible to make the best of this rainfall.

Unfortunately, few other Experimental Stations possess such complete masses of data as Rothamsted. Methods are now being devised, however, both by Fisher and by the able English investigator who modestly conceals his identity under the pseudonym "Student," for the study of smaller numbers of data, and it is hoped that these or others equally effective will be applied to the results of field experiments accumulated at various Experimental Stations throughout the world. A massed attack by a competent band of statisicians on the whole of the data of the best Experimental Stations, dealing with yields of crops under different conditions of nutrient supply, temperature, rainfall and other

factors that go to make up the aggregate called season, would yield information of extraordinary value.

Investigations of this kind, however, are necessarily slow, and they do not themselves afford complete information; their value lies in the fact that they reduce a very complex problem to a set of single-factor problems of the type with which the scientific investigator is already familiar. In the meantime, while this work is proceeding, much is being done by observational methods. At Rothamsted the field plots are under continual observation by a group of three workers, a physiologist, an ecologist, and an agriculturist, who study such factors as rate or habit of growth, earliness of starting or maturing, degree of resistance to insect or fungus attack; their observations are fully recorded and brought before the chemical, physical and botanical departments at regular and frequent intervals. Certain of the experiments are repeated at other centres on closely similar lines for purposes of comparison. In consequence our old field plots which have been studied for the past eighty years by Lawes, Gilbert, Warington, and Hall, and might have been supposed to have no further tales to tell, are found to be still yielding results of great interest in agricultural science and practice.

(*To be continued.*)

THE INSTITUTE OF METALS.

The Institute of Metals programme for the session 1924-25, which commences on October 1st, has just been issued. It covers not only the work of the parent institute, but of its six branches located in the various metallurgical centres. Over thirty important lectures dealing with various phases of non-ferrous metallurgy are enumerated in the programme, including the May Lecture by the distinguished Dutch Scientist, Professor H. A. Lorentz. Copies of the programme can be obtained from Mr. G. Shaw Scott, M.Sc., 36-38, Victoria Street, Westminster.

THE JUNIOR INSTITUTION OF ENGINEERS.

The 1924-25 session of the Junior Institution of Engineers will be opened on Friday, October 3rd, at 7.30 p.m., with a lecture on "Explosions, Terrestrial and Celestial," by Prof. A. W. Bickerton, A.R.S.M. The chair will be taken by Prof. H. J. Spooner, M.I.Mech.E.

A full programme of papers and lecturettes has been prepared for the year, covering a variety of subjects of present-day interest. On October 10th a paper entitled "The Design of Static Sub-stations" will be read by N. Thornton, A.M.I.E.E. (Member), and on October 17th, at a special meeting, a lecture on "High Voltage Electric Oscillations" will be delivered by R. P. Howgrave-Graham, M.I.E.E. Lecturettes to be delivered in October are "Powdered Fuel," by F. F. Evans (Member) on Friday, the 24th, and "Audio-frequency Transformers," by H. J. H. Riddle (Assoc. Member) on Friday, the 31st. The diary for October also includes two visits, one to a press tool factory and another to an optical lens works.

Further particulars of these meetings and tickets of admission may be obtained from the Secretary at 39, Victoria Street, S.W.1.

CORRESPONDENCE.

GEO-CHEMICAL PROBLEMS.

To the Editor of The Chemical News.

Sir,—May I add a few words in reference to the article entitled "The Sodium Cycle and Modern Geo-Chemical Problems," which appeared in your issue of September 12th? I said at the close that "certain regions are helpful" and have been discussing with a few friends the desirability of organising a small expedition in order to substantiate this statement. Geologists do not disagree on matters of theory without reason. Different parts of the world encourage different ways of looking at things. Now there is one broad distinction of parts which is known but not sufficiently known to chemists in general. Roughly speaking, the tropics encourage chemical ideas, the temperate zone mechanical ideas. "Weathering" preponderates in the one region, "erosion" in the other.

Splendid work has been done by geologists in the tropics, but they labour under a great disadvantage in discussion since the fundamental theories, and the language used, were worked out in the temperate zone.

Is there no way of bridging the gulf? I think there is, but it is not an easy one to describe. It demands co-operation and a broad outlook. I believe that some work

in the Mediterranean would illuminate the whole field of thought, and am looking for the means to carry out a preliminary attempt.

In the meantime, I hope criticisms and questions may be forthcoming in *The Chemical News.* They might help forward a piece of work of universal interest.

Yours,

J. H. GOODCHILD.

[The same plea is made, in more explicit terms, by the author of *Landscape and History*, recently reviewed in *The Chemical News* (1923, CXXVII, 335). The matter is certainly one of importance and would decide certain points of theory. It is to be hoped that there will be some response to Mr. Goodchild's request.—*Ed.*]

NOTICES OF BOOKS.

Technical Writing, by T. A. Rickard. Second Edition, pp. 337. New York. Wiley & Son; London: Chapman & Hall, Ltd. 1923. Price $2.00.

Mr. Rickard has had wide experience as an American Technical Editor. In this volume he gives a wealth of experience acquired in examining manuscripts for the press. He asserts that very little good literature is now read, whilst much time is spent on the piffle of the press. Even magazines rarely furnish safe models of writing and the ordinary text-book is but the "dry bones of a great art."

The book contains examples of incorrect grammar, bad English and jargon taken chiefly from technical publications.

As an example, the following is taken from a description of an Australian lode (p. 18):

"It may be considered as consisting of a network of veins, traversing on the one hand a metamorphic matrix of a somewhat argillo-arenaceous composition, and on the other hand what appears to be a feldspathic tufaceous igneous rock."

This is metamorphosed English pseudomorphic after flapdoodle. According to the author, much of the geologic description that poses as profundity is rhetorical rubbish.

On p. 56, Mr. Rickard states that the expression "11 cc. of iodine was used" is correct. This is contrary to the usual practice of chemical and other scientific journals in this country. His insistence that 11 cc. stands for "a quantity of 11 cc." does not alter the fact that centimetres requires a verb in the plural.

Neither will chemists endorse the statement that tungstate of lime is the best *terminology, although it is preferable to* lime tungstate.

The author is very scathing in regard to the superfluous use of superlatives. Other matters upon which useful information is given are the use of relative pronouns, prepositions, the misuse of words, punctuation and style.

To write in good English should be the aim of those who desire to present fresh facts and views to their fellow-scientists. This American book shows the way.

LITERARY INTELLIGENCE.

Messrs. J. & A. Churchill inform us that they have in the press, and hope to publish early in the New Year, a "Dictionary of Perfumery" by Ernest J. Parry, B.Sc., F.I.C., F.C.I. The work will be in two volumes. It will deal with the raw materials of the perfumery trade and with allied subjects from the point of view of the chemist, the manufacturer and the user.

Special articles, which will appear over the writers' signatures, have been contributed by Mr. A. C. Marrin (the Editor of the Perfumery and Essential Oil Record), Mr. C. T. Bennett, B.Sc., F.I.C., Mr. T. H. Durrans, M.Sc., F.I.C., Mr. M. Dewhirst, B.Sc., F.I.C., Mr. A. Garden, B.Sc., A.I.C., Mr. H. Salamon, B.Sc., F.C.S., and Mr. W. H. Simmons, B.Sc., F.I.C.

BOOKS RECEIVED.

A Systematic Course of Qualitative Chemical Analysis, by Henry W. Schimpf, Ph.G., M.D. Pp. IX. + 201. Fourth Edition. Messrs. Chapman & Hall, Ltd., 11, Henrietta Street, Covent Garden, W.C.2. 1924. 8s. 6d. net.

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

21496—Ellis G. H.—Manufacture of basic derivatives of the aromatic series. September 11th.

21182—Nilhoul, A.—Manufacture of magnesium salts. September 8th.

Specifications Published This Week.

199017—Koritschoner, Dr. J. and Hansgirg, Dr. F.—Method of manufacturing pure alumina.

221008—Kalle & Co. Akt-Ges.—Process of producing perylenetetracarboxylic acids of their mono-imides.

201906—Pollak, F.—Manufacture of condensation products from formaldehyde and urea, thio-urea, or their derivatives.

221000—Technical Research Works, Ltd., and Lush, E. J.—Process for the preparation and reactivation of metallic catalysts used in the hydrogenation of oils and like substances.

Abstract Published This Week.

218606—Electrolysis.—Ewan, T., 86, Shuna Street, Maryhill, Glasgow.

Sodium and potassium, obtaining; liquid-electrode apparatus.—A solution of the iodide of the metal required in liquid anhydrous ammonia is electrolysed with an amalgam of the metal as anode, the electrolyte being of such strength that as electrolysis proceeds it separates into two layers, the upper of which consists of a solution of the liberated metal, and the lower one of a solution of the salt. The upper layer is removed continuous and evaporated to give metallic sodium or potassium. Fresh ammonia and amalgam are supplied and the impoverished amalgam withdrawn continuously. The process may be carried out in apparatus similar to that described and claimed in Specification 218,563.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

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CRITICAL STUDIES ON METHODS OF ANALYSIS.

XII.—BORON.

By LEON A. CONGDON and J. M. ROSSO.
(*Contribution from the Department of Chemistry, Syracuse University*).

INTRODUCTION.

While boron as an element is not found free from other elements but as boric acid, borax, boracite, and colemanite, it is of great importance in the industries and medicine in the form of boric acid. A sure form of boron is obtained by reduction of the chloride with hot hydrogen, and the element has a special property in that its electrical resistance decreases enormously with rise in temperature, which no doubt could be made use of in automatic devices so prevalent in this century. The wide use of the compounds of boron has brought about considerable study for the estimation and detection since the discovery of the element by Davy in 1808.

The literature therefore shows some eighty original studies on the analytical chemistry of the element. Qualitative studies detect compounds of boron by means of the flame test which gives a decided green colour, the tumeric paper test which gives a red colouration, turning olive with dilute alkalies, the alcoholic extract of mimesa flowers test which with weak ammonia gives a red colouration, the borax bead test plus cobalt solution gives a coloured blue bead, and the formation of volatile ammonium boroflouride test.

The greater part of the quantitative study for boron and its compounds takes up the volumetric neutralization process, where it has been found that boric acid cannot be titrated by means of the ordinary indicators on account of its feeble ionization, hence the addition of glycerine or other substance which forms with the acid a complex which is more highly ionized than the boric acid itself. The other substances studied other than glycerine which gives approximately the same complex are mannitol, sodium ethoxide in alcoholic solution, fructose, etc.

Gravimetric studies for the estimation of boron and its compounds depend on the following principles. *1st.* On distillation methods, we have the formation of volatile methyl borate and fixation by lime or by sodium tungstate, the increase in the weight of the lime or sodium tungstate when dried, ignited, and weighed gives the B_2O_3 in the sample. *2nd.* A modification of the distillation method where ammonium carbonate is substituted for the CaO for fixation of the volatile methyl borate and the formation of boron phosphate by evaporation with ammonium hydrogen phosphate, this heated finally at a high temperature in an electric furnace to 1000° and the boron weighed as boron phosphate. *3rd.* The formation of $Ca_3(BO_3)_2$ with $CaCl_2$ in a fused chloride salt solution, and separation of BO_3,CaO in which form it is weighed. *4th.* The estimation of boric acid by drying the solution with $CuSO_4$, extracting with alcohol, running the filtrate into standard baryta solution, and converting the excess of baryta with carbonate by passing CO_2 through the solution, evaporation of the solution and weighing the $BaCO_3$, thus indirectly finding the per cent. of boron or boracic acid. *5th.* By treating the boron compound with NH_4F to volatilize the boron as ammonium boroflouride, then adding H_2SO_4, evaporation under hood, and igniting, finally weighing the residue, the difference from the first and last weight of substance being the boron. *6th.* By precipitating as double boron and potassium flouride by KOH and HF, evaporation to dryness, and treating the mass with a concentrated solution of potassium acetate to

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remove other salts, filtering, then the precipitate is washed with a solution of potassium acetate. Finally, the precipitate is washed on the filter with alcohol to remove the acetate of potash, then dried at 100°, and weighed as KBF_4. *7th.* Estimation of boric acid by weighing as calcium borate crystals.

Colorimetric estimation of boron is based on the color of boric acid solution with curcumin, by turmeric paper tints, and by using an ethyl acetate solution of turmeric giving tints in accordance with the amount of boron present.

Numerous studies have been made on the estimation of boron in various products such as iron and steel, glass and silicates, milk, ashes, salves, etc.

For this particular study, selection has been made of four methods—three of which are gravimetric ones and one volumetric method. The gravimetric methods are:—Gooch's (1) process by formation of volatile $(CH_3)_3BO_3$ and fixation by lime; Aschman's (2) phosphate method; and Ditte's (3) $Ca_3(BO_3)_2$ method by formation with $CaCl_2$ in a fused salt solution. The volumetric method is:—Dunstan's (4) neutralization process with addition of glycerine.

Principles of the Methods Used.

(1) F. A. Gooch's process depends upon the fact that borates of alkaline earths and alkalies give up their boron in the form of the volatile methyl borate when they are distilled with absolute methyl alcohol which is acetone free. The methyl borate, b.p. 65°, passed over lime in presence of water is completely saponified, the liberated boric acid combining with the lime to form calcium borate, which may be dried, ignited, and weighed. The increase of the weight of the lime representing the B_2O_3 in the sample. The equation is represented as follows:—

$$2B(CH_3O)_3 + CaO + 6H_2O = 6CH_3OH + Ca(BO_2)_2 + 3H_2O.$$

(2) Ashman's process is based on the same principle as Gooch's method but is especially suitable for the determination of boron in steel. The boron is weighed as boron phosphate, BPO_3. The procedure is the same as that of Gooch, except the receiver for the methyl borate contains a solution of ammonium carbonate instead of the calcium oxide solution used by Gooch. After the distillation is over, the distillate is evaporated in a platinum dish containing one gram of $(NH_4)_2HPO_4$. After dryness is reached, the residue is gradually ignited and then heated to constant weight in an electric or muffle furnace for two days.

(3) Ditte's method is based on the partial solubility of calcium borate in a hot melted saline solution at a lower temperature. The method is claimed to be suitable for samples containing boracic acid alone or in combination with alkaline oxides. The procedure calls for a little ammonia added to the solution in order to neutralize any free acid and then an excess of a saturated solution of pure calcium chloride. The boric acid is precipitated in a form of a gelatinous precipitate, $Ca_3(BO_3)_2$, soluble in a heated $CaCl_2$ solution in excess. The material is now introduced in a platinum dish and evaporated to dryness. When dry, it is transferred to a platinum crucible with the aid of a little water, and then heated again until dry. The crucible is then filled with a mixture of crystals of NaCl and KCl (in equivalent proportion) and heated moderately at first and then to fusion, taking care to prevent loss by spattering. The $Ca_3(BO_3)_2$ collects at the bottom of the crucible in a spongy mass. At the bottom of the crucible, a temperature higher than that at the top is maintained, and the dissolved $Ca_3(BO_3)_2$ crystallizes on the surface of the mass and forms a ring. When all of the borate is converted in this ring and nothing remains on the bottom of the platinum crucible, the material is allowed to cool and is then separated from the receptacle. After separation, the $Ca_3(BO_3)_2$ is mixed with a little cold water to dissolve any chlorides, then slightly warmed and left to crystallize, and finally filtered, washed with cold water, detached from the filter after drying, and weigheda s $Ca_3(BO_3)_2$.

(4) Dunstan's neutralization process with addition of glycerine takes advantage of the fact that boric acid reacts neutral to methyl orange and may be quantitatively titrated in the presence of glycerol, which prevents the hydrolysis of the weak boric acid. There has been many modifications suggested for this method. In this study, N/2 NaOH solution was used and added from a burette to a solution of the boric acid plus 50 cc. of glycerol until a change was observed by means of phenolphthalein as indicator. More glycerol was then added, and the titration continued with N/2 NaOH until a point was reached when the color did not fade when new portions of glycerol were

added. From this titration, the equivalent weight of boric acid is calculated.

EXPERIMENTAL.

The sample used with all methods was c.p. boric acid, containing a trace of sodium, 0.001 % of Cl, 0.001 % of SO_3, and no lead or CaO present. The sample was weighed out by means of a ground glass stoppered weighing bottle. The following table gives the results of analysis:—

Method.	Weight.	Theor. B_2O_3 per cent.	Aver. B_2O_3 per cent.	Difference per cent.
Gooch's Distillation Gravimetric $Ca_3(BO_3)_2$.	0.1795 0.3450	56.45	56.36	-0.07
Aschman's Distillation Gravimetric Phosphate.	0.1621	56.45	55.35	-1.10
Ditte's Gravimetric $Ca_3(BO_3)_2$.	0.1491	56.45	55.00	-1.45
Dunstan's Volumetric Glycerol Neutralization	0.2299	56.45	56.45	0.00

SUMMARY AND CONCLUSIONS.

1. The study of these methods for boric acid shows that their accuracy can be classified as follows, the most accurate coming first:—1st, Dunstan's volumetric neutralization process with addition of gylcerol; 2nd, Gooch's distillation gravimetric $Ca_3(BO_3)_2$ method; 3rd, Ashman's distillation gravimetric phosphate procedure; and 4th, Ditte's gravimetric $Ca_3(BO_3)_2$ method.

2. The quickest and most accurate method for the determination of boric acid is that originally devised by Dunstan and later modified by a number of investigators. This method is based on the fact that glycerol prevents the hydrolysis of the weak boric acid and hence it can be titrated volumetrically with standard alkali using a suitable indicator.

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(1) Gooch, F. A.; *Proc. Amer. Acad. Arts & Sci.* 1886, XXII., 167; *Amer. Chem. Jour.*, 1887, IX., 22. (2) Ashman; *Jour. Soc. Chem. Ind.*, 1916, 1263. (3) Ditte, M. A.; *Compt. rend.*, 1875, VII., Feb. 22nd; *Chem. News*, 1875, XXXI., 150. (4) Dunstan, W. R.; *Pharm.*, 1882, III., 13, 257; Beythein, A. and Hemple, H.; *Zeit. Untersuch. Nahr. Genuss.*, 1899, II., 642; Biltz, W. and Marcus, E.; *Zeit. Anorg. Chem.*, LXXVII., 131; Cepeaux, M.; *Compt. rend.*, 1895, CXXVII., 756; Deniges, G.; *Jour. Pharm. Chem.*, 1897, VI.; Donath, E.; *Chem. Zeit.*, 1893, XVII., 1826; Farrington, E. N.; *Rev. Internat. Falsif.*, 1897, X., 81; Farnsteiner, K.; *Zeit. Untersuch. Nahr. Genuss.*, 1902, V., 1; Fischer, B.; *Zeit. Untersuch. Nahr. Genuss.*, 1900, III., 17; Gasselin, V.; *Ann. chim. Phys.*, 1884, VII., 1; John, K.; *Arch. Pharm.*, 1887, XXV., 250; and Jones, E. C.; *Amer. Jour. Sci.*, 1898, 147-153.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

A General Meeting was held at the House of the Royal Society of Arts, on Tuesday, 7th October, 1924. Paper read—

Recent Developments in the Art of Cracking, by A. E. DUNSTAN, D.Sc., F.I.C., F.C.S., M.Inst.P.T.

The chair was taken by the President, H. Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst.Mar.Eng.

THE STRUCTURE OF SILVER.

By HAWKSWORTH COLLINS, B.A. (Camb.)

By the application of the five main principles in the constitution and structure of the chemical elements (*The Chemical News*, 1920, CXXI., 183) an atom of Ag (107) was shown to be formed by the union of one of As (75) with one of S (32), the five valences of the former being neutralised by five of the six valences of sulphur, leaving one free, so that Ag is a monad. This must be an electro-positive force, as there is 1 0 free H + H_3.

The molecule As_2S_3 (= $As_2S_2.S$ = Ag_2S) is found intimately associated with the molecule Ag_2S in mineralogy.

This structure for an atom of silver will now be proved to be correct quite independently by means of the laws of relative volume and heat of formation.

TABLE I.

The Relative Volumes of Silver.

Ag	=	As			+	S
Ag	=	C	+	Cu	+	S
9.78	=	0.71	+	9.07	+	0
10.25	=	0.71	+	9.54	+	0
13.29	=	0.71	+	9.54	+	3.04

The volumes 9.07 and 9.54 for Cu were demonstrated in *The Chemical News*, 1924, CXXIX., 157; and 3.04 for sulphur in the paper on cobalt, 1924, CXXIX., 107.

TABLE II.

Experimental Data illustrating Table I.

		Relative Volume.	Theor. S.G. at 15° C.	Obs. S.G.
(249)	Ag_4Sn	4(9.78) + 16.02	9.9	9.95 15° Holzmann
(250)	$AgSn_2$	9.78 + 2(16.02)	8.2	8.223 16° Holzmann
(251)	$AgSn_3$	9.78 + 3(16.02)	7.97	7.936 19° Holzmann
(252)	$AgSn_6$	9.78 + 6(16.02)	7.69	7.666 18°.4 Holzmann
(253)	$AgPb_4$	9.78 + 4(18.17)	11.29	11.196 21° Matthiessen
(254)	$AgPb_{10}$	9.78 + 10(18.17)	11.32	11.285 22° Matthiessen
(255)	$AgPb_{25}$	9.78 + 25(18.17)	11.33	11.334 20°.6 Matthiessen
(256)	Ag	10.25	10.44	10.4476 Baudrimont
(257)	Ag	10.1	10.6	10.621 0° Quincke
(258)	*Au_6Ag*	*7(10.25)*	*18.0*	*18.04 13° Matthiessen*
(259)	Au_4Ag	5(10.25)	17.5	17.54 12° ,,
(260)	Au_2Ag.	3(10.25)	16.3	16.344 13° ,,
(261)	AuAg	2(10.25)	14.83	14.87 13° ,,
(262)	$AuAg_2$	3(10.25)	13.4	13.43 14° ,,
(263)	$AuAg_4$	5(10.25)	12.2	12.257 14°.7 ,,
(264)	AgI	10.25) + 32.77	5.44	5.47 0° Deville 5.35 Schiff
(265)	$Ag_5I.Br_2Cl_2$	5(10.25) + 27.75 + 2(23.09) + 2(15.085	5.736	6.152 0° Rodwell 5.713 18° Lasaulx
(266)	Ag_5I_3BrCl	5(10.25) + 3(27.75) + 2(23.09) + 2(15.085)	5.970	5.9717 0° Rodwell
(267)	Ag_3PO_4	3(10.25) + 14.56 + 4.45 + 3(2.51)	7.26	7.321 Stromeyer
(268)	CuAgS	7.13 + 10.25 + 15.53	6.14	6.15 Dana
(269)	*Ag_2S*	*2(10.25) + 15.53*	*6.83*	*6.85 Karsten*
(270)	AgCl	10.25 + 15.085	5.62	5.59 Schroder
(271)	Ag_2Se	2(10.25) + 16.27	7.94	8.0 Rose
(272)	$Ag_2S.Bi_2S_3$	2(10.25) + 15.55 + 2(21.29) + 3(10.51)	6.90	6.92 Rammelsberg
(273)	AgI	13.29 + 27.75	5.702	5.707 Damour
(274)	$AgNO_3$	13.29 + 3.8 + 3(7.53)	4.26	4.253 – 4.27 Schroder
(275)	Ag_2O	2(13.29) + 2.51	7.9	7.521 Schroder 8.26 Karsten
(276)	Ag_2S	13.29 + 10.25 + 10.51	7.225	7.24 Chem. Kal.

(277)	$Cu_2Ag_2Se_2$	2(5.23) + 10.25 + 13.29 + 2(16.27)	7.45	7.48 Nordenskiold
(278)	Ag_2Cl_2	10.25 + 13.29 + 2(15.085)	5.31	5.31 Domeyko
(279)	Ag_2SO_4	2(13.29) + 30.59	5.422	5.425 Schroder
(280)	$Ag_2SO_4 + 4NH_3$	2(13.29) + 30.59 + 4(18.11)	2.917	2.918 Playair & J.

The volume 10.1 which has previously been given for metallic silver is a mixture of the two volumes 9.78 and 10.25. The word ' metallic ' in this and other cases is intended to denote the element in the alloyed state as well as in the uncombined state.

TABLE III.

Heat of Formation of Silver.

		H.F.	Original Volume.		Rel. Vol. in combination at 15° C.		Change of Volume
-45080	=	120 × (-3.51) × 107	9.78	=	13.29	-	3.51
0	=	120 × 0 × 107	10.25	=	10.25	-	0
liq. -50300							

TABLE IV.

Experimental Data Illustrating Table III.

Heat of Formation.			Theor.	Obs.
Ag_2O	- 2(45080) + 96155	=	5995	7000. 5900 T
(Corresponds with No. 275, Table II.)				
$AgNO_3$	- 45080 - 23300 + 3 (32341)	=	28643	28700
(Corresponds with No. 274, Table II.)				
KNO_3	37274 - 23300 + 3(32341)	=	110997	110700
Ag_2S	- 45080 - 0 + 49959	=	4879	3000. 3330 T
(Corresponds with No. 276)				
Ag_2Br_2	- 45080 - 0 + 2(45244)	=	45408	45400
Ag_2I_2	- 45080 - 0 + 2(36226)	=	27372	27600
(Corresponds with Nos. 264 & 273 together).				
Ag_2SO_4	- 2(45080 + 0 + 2(96155 + 32341)	=	166832	167100
$Ba(NO_3)_2$	81926 + 2(-23300 + 3(32341)	=	229372	228400
$BaBr_2$	81926 + 2(45244)	=	172414	172100
$Ag_2.O_2.N_2O_4$	2(-45080 + 32341) + 85332	=	59854	60130
$aq.Ag_2.O.\ N_2O_5$	2(-50300) + 32341 + 85332	=	49414	49250
$aq.Ag_2.O.\ N_2O_5$	2(-50300 + 32341) + 85332	=	17073	16780

The heat evolved, 85332, when N_2O_4 and N_2O_5 become portions of inorganic molecules, cannot be explained until N is onsidered.

SUMMARY.

By reasoning upon atomic weight, valency, and the facts of mineralogy, the constitution of Ag was found to be AsS (= CuCS) and was first published as such in an advertisement in *The Chemical News*, 1910, CI.

This deduction is now proved to be correct.

(1) by the fact that each of the three volmes of Ag can be split up into parts which have previously been demonstrated to be volumes of Cu, C and S, any of which may be zero in accordance with the law of relative volume;

(2) by the fact that each of the combining volumes produces by the law of heat of formation a correct value for the heat of formation of Ag.

SODIUM TUNGSTATE.

By Edgar F. Smith.

(Contribution from the John Harrison Laboratory of Chemistry—University of Pennsylvania.)

(*Continued from Page* 209).

All the observations here cited had been repeatedly confirmed in the experimental way by the writer, who continued to view the 5:12-salt as a double salt. He, too, used large quantities of it and subjected them to careful treatment with water. Thus—

Experiment 1. 1.6 grams of fused 5:12-salt were covered with 200 cc. of water and allowed to stand for five hours. The insoluble residue amounts to 70.5% of the original fused mass and the portion which dissolved equalled 20.5%.

Experiment 2. On treating 1.41 grams of the fused material with 300 cc. of water—applying the latter in five portions of 60 cc. each; the residue amounted to 73.97%, while the portion which passed into solution equalled 26.03%.

Experiment 3. Two grams of the fused substance were permitted to stand for seventeen hours in contact with 500 cc. of water. The insoluble residue proved to be 76.99% of the original, while the soluble portion equalled 22.59%.

Experiment 4. Here the conditions were perfectly similar to those of Experiment 3, with the result that the insoluble part was 75.25% of the original and the soluble part 24.69%.

If arranged into soluble and insoluble residues they appear as follows:

	Soluble Residues and	*Insoulbe Residues*
1.	29.5 %	70.5 %
2.	26.03%	73.97%
3.	22.59%	76.99%
4.	24.69%	75.25%
Mean	26.20%	73.67%

Assuming that these molecules of the 5:12-salt would give eight molecules of the normal (1:1) and seven molecules of the meta(1:4)-salts,

3 (5 Na_2O. 12 WO_3) 8 (Na_2O. WO_3) + 7 (Na_2O . 4 WO_3) the theoretical requirements of the fused 5:12-salt would be 74.73% insoluble salt (fused 1:4) and 25.27% of soluble salt (fused 1:1).

This is, of course, only an approximate separation, but, in a singular way, it confirms the later synthetic and hydrolytic experiments.

The literature of the alkali tungstates abounds, as previously observed, with references to their ready hydrolysis. To it was attributed many of the difficulties encountered in their study, to which there is ample allusion by Wolcott Gibbs, indefatigable student of innumerable derivatives of tungsten. Some experiments, germane to this point, therefore, follow:

1. Five grams of the 5:12-salt were dissolved in a liter of water, and the solution boiled for three hours. It was allowed to cool to a temperature of 75° C., when 300 cc. of hydrochloric acid (1:3) were added. In a few minutes the tungstic acid separated out. It was filtered and washed as well as was possible with such a gelatinous, voluminous mass. After drying it was ignited, and on cooling the residue weighed 0.8750 gram.

The filtrate from the precipitated tungstic acid was evaporated. The acid which separated out was collected, washed and ignited. It weighed 2.9514 grams.

On the basis that 3 molecules of the 5:12-salt consisted of 8 molecules of normals odium tungstate—8 (Na_2O. WO_3 + 2 H_2O), and 7 molecules of the sodium metatungstate, the tungstic acid present in the normal salt (1:1), contained in five grams of the 5:12 salt, should be 0.860 gram, and the tungstic acid of the meta portion 3,000 grams. Therefore, there is a very good approximation in results.

A second experiment, with conditions precisely like those set forth in the preceding example, gave:

0.8749 gram WO_3, corresponding to the normal salt,

and 2,9781 grams WO_3, from the meta portion of the salt.

In a third trial 0.8680 gram tungstic acid, corresponding to the normal salt in the 5:12, was obtained, while the portion of acid from the meta-salt weighed 2.9583 grams

Found WO_3 from normal salt	Theoretical WO_3 from normal salt
0.8750 gram	0.8600 gram
0.8740 ,,	
0.8680 ,,	0.8600 ,,

Found WO_3 from normal salt	Theoretical WO_3 from meta salt
2.9514 grams	3.0000 grams
2.9781 ,,	3.0000 ,,
2.9583 ,,	3.0000 ,,

In cold solutions of the 5:12 salt, the precipitation of the tungstic acid was very incomplete. Hydrolysis had not been carried to its conclusion; but in all instances where the 5:12-salt solution had been boiled, even for a period of five minutes or less, the results were similar to those detailed above. Many other examples of complete hydrolysis, with their quantitative results, might be given. All confirmed the first results and favoured the requirements, called for by a formula 8 (Na_2O. WO_3) + 7 (Na_2O . 4 WO_3) + Aq.

Inasmuch as the complete dydrolysis of 5:12 was so easy, a zinc salt, in excess, was added to the boiled liquid containing a definite quantity of 5:12-salt. A precipitation ensued and the weighed zinc tungstate pointed to a satisfactory quantitative result. However, further attempts in this direction proved too unsatisfactory to offer the method as in any way demonstrating the point under consideration. On substituting cadmium sulphate as a precipitant, the result was gratifying, as shown in one of many determinations conducted in this fashion.

Experiment: Three grams of 5:12-salt were dissolved in 250 cc. of water, and the solntion boiled. A boiling solution of cadmium sulphate in excess was next introduced and the cadmium tungstate immediately filtered, washed, dried, ignited and weighed.

Supposing the 5:12-salt to consist of 8 molecules of the normal and 7 of the metatungstate, the WO_3 from the normal would be 0.5171 gram, while that found in this particular trial amounted to 0.5171. The quantity of tungstic acid belonging to the meta-salt in this determination would be 1.8100 grams, while that actually found weighed 1.7930 grams.

Reviewing the evidences given by the analyses of the fused 5:12-salt and the products of its hydrolysis, the salt contains the normal sodium tungstate and the meta-salt in the proportion of eight molecules of the first to seven of the second, equivalent to a ratio between them of 1:3.1, or in other words, if 10 grams of the 1:1-salt and 31 grams of the 1:4-salt were brought together in 20 to 30 cc. of water, after solution and standing over night the salt 5:12 would appear. This occurred many times. The synthetic product had all the characteristics of the salt made in the ordinary way. Little attention was given this synthesis by von Knorre (Berichte, *18*, 326 and 2362); indeed, as little as was shown by most students of the sodium tungstates who, in the preparation of the meta-salt (1:4), had observed the frequent appearance of the 5:12-salt in their work. For example, if without proper consideration of the quantities of tungsten trioxide required for the conversion of the normal salt into 1:4-salt *they had added an insufficiency of the* tungstic acid.

Synthetic 5:12-salt (5 Na_2O . 12 WO_3 . 28 H_2O) contains:

14.01%	H_2O
77.38%	WO_3
8.61%	Na_2O

Two out of the many analyses of the synthetic product showed:

13.92%	13.92%	H_2O
17.47%	17.49%	WO_3
8.61%	8.59%	Na_2O

Pause now for a moment, and consider the 5:10-salt. Is it a combination of the normal 1:1 with the 1:4? It was noticed several times in the tungstation of normal sodium tungstate, in the effort to get sodium mea-tungstate. Yes,

$$6\ (Na_2O\ .\ WO_3 + 2H_3O) + \underset{\text{normal}}{}\ 6\ (Na_2O\ .\ 4WO_3 + 9.5\ H_2O)\ \underset{\text{meta}}{}$$

would theoretically yield

$$3\ (4\ Na_2O\ .\ 10\ WO_3 + 23\ H_2O).$$

Such being the case, weighed quantities of the 4:10-salt were fused and tested as to their solubility. They proved to be wholly analogous to those obtained with the 5:12-salt. Again, on hydrolysis, the outcome was as recorded with the 5:12-salt. All indicated that 1:1 and 1:4 were contained in the above equation-ratio, or as 1 part of normal to 3.54 parts of the meta-salt, and upon bringing the components together in this proportion in water, after a few hours, *beautiful crystals of the* 4:10-salt appeared.

(To be continued.)

GENERAL NOTES:

GOVERNMENT CHEMISTS RESEARCH.

The Government Chemist issues an interesting report of important work done for the year ended March 31st, 1924, by the Government Laboratory. It deals with the activities of the Laboratory in connexion with the Admiralty, Ministry of Agriculture and Fisheries, Air Ministry, Colonial Office, Crown Agents for the Colonies, Board of Customs and Excise, Geological Survey, Ministry of Health, Board of Inland Revenue, Ministry of Pensions, Post Office, Department of Scientific and Industrial Research, Home Office, Board of Trade, War Office, Office of Woods and Forests, Privy Council, and Office of Works.

The total number of samples examined in the course of the year was 390,421, as compared with 343,453 in the preceding year—an increase of 46,968. There has been an increase of more than 21,000 in the number of samples examined at the chemical stations, while the number examined at the central laboratories in London had risen from 225,073 to 251,000—an increase of 25,936.

Following the examination of some old mortars and plasters for durability, the opinion is expressed that there is no reason, from the information available, why well-constructed, modern buildings should not last as well as ancient buildings of similar character still surviving. The treatment of some old tiles at the Chapter House at Westminster seemed to be effective, since the tiles now present a good appearance and their designs are well brought out. The unique wall paintings in the Chapter House had been examined, and a process of cleaning had been suggested which is free from objection so far as injury to the paint is concerned. One or two small panels had been cleaned with good results in bringing out the detail hidden under dirt. It was hoped to treat the surface of the paintings in such a manner as to prevent further flaking, and at the same time keep the surface in its original state, apart from the natural loss of brilliancy due to age.

SCIENTIFIC CONSERVATION OF COAL.

The Annual Conference of the British Commercial Gas Association was opened at Liverpool on September 30th. The Association is important and represents no less than 773 gas undertakings responsible for 92 per cent. of the total gas output of the country.

Alderman C. H. Rutherford, in the absence of the Lord Mayor, welcomed the conference. The introduction of water in gas manufacture, he said, had helped to purify and cheapen gas, though it might have made it more dangerous to human life. Parliament and local authorities therefore required makers of gas to reintroduce "some of the stinking stuff" that escapes might be traced immediately.

Mr. H. W. Deacon (the President of the Association), in his address, emphasized as one of the advantages of gas fires and cookers the absence of smoking chimneys. He also stressed the fact that we had not in this country the advantages of the great supply of water power possessed by some of our competitors in other countries. Consideration of the possibilities of obtaining such power in quantity by damming the Severn was, he said, only now entering upon its early stages. We had no oil wells. Our only present source of power was coal, and as our stores of coal were being used up rapidly, it was necessary in the national interests that the utmost possible use should be made of the coal we had.

We must learn to understand the distinction between power and heat. Power must be restricted to mean "motive power" when we considered "power schemes." The problem of coal conservation comprised two separate considerations:—

(1) The economic utilization of coal as a source of smokeless, labour-saving *motive power*; and

(2) The economic utilization of coal as a source of smokeless, labour-saving *fuel*.

While the answer to the one might be largely—it was by no means wholly—"electricity," the answer to the second was almost entirely "gas and coke." He believed that the more extended the use made of gas in manufacturing operations, the better would our manufacturers be able to meet the growing competition for the trade of the world.

SCIENTIFIC RESEARCH AND THE SMOKE EVIL.

The Committee and Privy Council for Scientific and Industrial Research has issued its report for 1923-24, and it constitutes interesting reading both for the scientist and the man in the street. During the period covered by the report, August 1st, 1923, to July 31st, 1924, recommendations were received from the Advisory Council on the programme of research for 1924-25, for which and for administrative services net estimates had been drawn amounting to £328,281, as compared with £276,863 for 1923-24.

During the academic year 1923-24, 291 grants were made to research workers and students in training, involving an expenditure of £41,000, compared with £49,000 in the previous year. The expenditure of the Department on headquarters administration during the financial year 1923-24 was £33,367. The total expenditure of the Department during the financial year 1923-24 was £515,382. This sum was made up of £274,297 from the Exchequer, £42,761 from the interest of the Million Fund, £103,187 from the capital of the fund, and £85,251 from fees for tests and special investigations for outside bodies, &c.

The report of the Advisory Council contains a mass of informations, one of the outstanding features being the work of the Fuel Research Board. In connexion with this, the Council say they consider that a sum of from £20,000 to £30,000 per annum, in addition to the present expenditure of the Board, would be fully justified for the various purposes which are outlined. The Council add:—"Meantime much can be done, and must be done, to prevent waste and diminish the smoke evil. Proper fuel control in industrial wors would have considerable effect in this direction, and without it the advantages of the better fuel which research may provide would be largely nugatory."

Good progress had been made during the year at the National Physical Laboratory. Among the more recent researches undertaken was an investigation directed towards the eventual adoption of a wave-length of light as a standard of length. The principle of the ultimate use of a wave-length of light as the primary length standard had been recognized by a recent decision of the Comité International des Poids et Mesures, and the matter had in consequence become of fundamental importance for the laboratory.

The maintenance of standards also comes under review, and it is stated that another subject of great importance to which much attention had recently been given was the realization of an international temperature scale. Good progress had been made with the aeronautical researches for the Air Ministry, includiug, especially, the problems of stability and control of aeroplanes when flying at low speeds. Interesting developments had also been made in aerodynamical theory as applied to aircraft problems, which might have far-reaching effects in the future in the simplification of methods of design.

The most important event of the year, so far as the work of the Food Investigation Board was concerned, was the sending of a small scientific expedition to Australia to study the conditions of apple transport to this country. The duty of the expedition was to obain records of, and to study minutely, the composition of the atmosphere, the humidity, &c., obtaining in a ship's hold carrying apples; to test various types of instruments for measuring temperature and humidity so as to obtain a critical estimate of their suitability for use at sea.

The work of the Fruit and Vegetables Committee now covered a wide field; and great importance was attached to the commercial storage trials conducted under rigorously controlled conditions. Laboratory researches had been continued at Cambridge and at the Imperial College of Science and Technology, London.

The apparatus developed at the National Physical Laboratory for the measurement of the strength of received radio signals had been completed, and sets of apparatus had been erected at four places in Great Britain, where observations on signal intensity were now being carried out. The strength of the signals sent out under the auspices of the International Union from European transmitting stations was being measured each day, and data of considerable interest were being collected. An endeavour was being made through the British National Committee of the above union to arrange for an increase in the number of stations transmitting signals suitable for measurement.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE BRITISH ASSOCIATION.

[Toronto Meeting.]

Presidential Address to Section M.—Agriculture, by Sir E. John Russell, F.R.S., entitled *Present-day Problems in Crop Production.*

(*Continued from Page* 216.)

The Results Obtained: Alterations in the Plant.

We shall begin with the results obtained by affecting alterations in the plant. Reference has already been made to the changes brought about by the plant breeder, and we need not stop to argue whether the great improvements in crops made in pre-Mandelian days by the Suttons and Findlay in potatoes, by Chevalier in barley, by the Gartons in oats, Vilmorin in sugar beet, and others, should be labelled empirical or scientific. There are certain other changes in plants, however, of a purely temporary nature, which have been induced by changes in conditions. It is a commonplace among farmers that certain soil conditions influence not only the yield but also the quality of crops. The leaf and root are more easily affected than the seed. The case of mangolds has been investigated at Rothamsted; the sugar content of the root, an important factor in determining feeding value, was increased by increasing the value of potassium to the crop. Middleton at Cockle Park showed that grass increased in feeding value—quite apart from any increase in quantity—when treated with phosphates. Potatoes are considerably influenced by manuring; increasing the supply of potassium influences the composition of the tubers and also that much more inpalpable quality—the cook's estimate of the value of the potato; while we have found at Rothamsted that a high-class cook discriminated between potatoes fertilised with sulphate of potash and those fertilised with muirate of potash, giving preference to the former.

Grain is more difficult to alter by changes in environment conditions; indeed, it appears that the plant tends to produce seed of substantially the same composition whatever its treatment—with the important exception of variation in moisture supply. Mr. Shutt has explored the possibilities of altering the character of the wheat grain by varying the soil conditions, and finds that increases in soil moisture decrease the nitrogen in the grain. Similar results have been obtained in the United States.

On the other hand, in England the reverse seems to hold, at any rate for barley. This crop is being fully investigated at the present time under the Research Scheme of the Institute of Brewing, because of its importance in the preparation of what is still Britain's national beverage. Increased moisture supply increases the percentage of nitrogen in the grain, and so also does increased nitrogen supply, though to a much less extent; on the other hand, both potassic and phosphatic fertilisers may decrease the percentage of nitrogen, hough they do not always do so; the laws regulating their action are unknown to us.

The practical importance of these problems of regulating the composition of the plant lies in the fact that the farmer can control his fertiliser supply, and also to some extent his moisture supply, so that it lies within his power to effect some change should he wish to do so.

The following are the nitrogen contents and the valuations of barley grown in the same lot of seed on farms only a few miles apart:—

Effect of Moisture.

	Drier soil	Moist land
Nitrogen per cent. in grain	1.44	1.80
Valuation per quarter of 448 lb.	52s. 5d.	41s. 6d.

Effect of Nutrients.

	No nitrogenous manure	Nitrogenous manure
Nitrogen per cent. in grain	1.379	1.464
Valuation per quarter of 448 lb.	53s.	52s.

At present we know but little about the matter and we are not in a position to advise the farmer as to how he may use these facts to the full advantage. The complete study of the problem necessitates the co-operation of a plant physiologist.

There is another direction also in which alterations in the plant would be of great

value if only we knew with certainty how to bring them about.

In agricultural science one sometimes thinks only of the crop and the factors that affect its growth. But in agricultural practice there is often another partner in the concern: a pest or parasite causing disease. The amount of damage done by pests and diseases to agricultural crops is astounding; in Britain it is probably at least 10 per cent. of the total value of the crops and the loss is probably some 12,000,000*l*. sterling per annum; in some countries it is considerably more. Indeed, the number of insect pests and of harmful fungi and bacteria that skilled entomologists of mycologists have found in our fields might almost lead us to despair of ever raising a single crop, but fortunately the young plant, like the human child, grows up in spite of the vast number of possible deaths. The saving fact seems to be that the pest does harm only when three sets of conditions happen to occur together; the pest must be present in the attacking state; the plant must be in a sufficiently receptive state; and the conditions must be favourable to the development of the pest. It is because this favourable conjunction of conditions comes but rarely that crops manage to survive. And this gives us the key to control if only we knew how to use it. Complete control of any of these three conditions would end all plant diseases. Unfortunately, control is never complete even in glasshouse culture, still less out of doors. But even partial control would be very helpful. All these pests go through life cycles, which are being studied in great detail all over the world, and especially in the United States. Somewhere there occurs a stage which is weaker or more easily controlled than others, and the pest would become harmless if the chain could be broken here or if the cycle could be sufficiently retarded to give the plant a chance of passing the susceptible stage before it is attacked.

The plants themselves, as we have just seen, are in some degree under control, and if they could be pushed through the susceptible stages before the pest was ready they fly (*Chlorops tœniopus*). The larvæ emerge in spring from the eggs laid on the leaves and invariably crawl downwards, entering the young ear if, as usually happens, it still remains unsheathed in leaves. J. G. H. Frew, at Rothamsted, has shown that early sowing and suitable manuring cause the ear to grow quickly above the track of the larvæ, and thus to escape injury. E. A. Andrews, in India, has found that tea bushes well supplied with potassic fertiliser escape attack from the mosquito bug (*Helopeltis*) for the rest of the season, apparently because bushes so treated become unsuitable as food to the pest. And further, the conditions are alterable. H. H. King, in the Sudan, has effected some degree of control of the cotton thrips (*Heliothrips indicus*) by giving the plant protection against the drying North wind and so maintaining a rather more humid atmosphere—a condition in which the plant flourishes more than the pest. Tomatoes in England suffered greatly from *Verticillium* wilt till it was found that a small alteration of temperature threw the attack out of joint. They are also much affected by stripe-disease (*B. lathyri*), but they become more resistant when the supply of potash is increased relative to the nitrogen. It has recently been maintained, though the proof is not yet sufficient, that an altered method of cultivating wheat in England will afford a good protection against bunt. These cultural methods of dealing with plant diseases and pests offer great possibilities, and a close study jointly by plant physiologists and pathologists of the responses of the plant to its surroundings, and the relationships between the physiological conditions of the plant and the attacks of its various parasites, would undoubtedly yield results of gerat value for the control of plant diseases. Again, however, the plant breeder can save a world of trouble by producing a variety resistant to the disease ;or there may fortunately be found an immune plant from which stocks can be had, as in the case of the potatoes found by Mr. Gough to be immune to the terrible wart disease.

CONTROL OF ENVIRONMENT FACTORS.

It thus appears that, if only plant breeders and plant physiologists could learn to alter existing plants or to build up new plants in such a way that they should be well adapted to evisting soil and climate conditions, and not adapted to receive disease organisms at the time the organisms are ready to come—if only they could do this all agricultural land would become fertible stages before the pest was ready they come ineffective: at any rate until the pests tile and plant diseases and pests would beadapted themselves to the new plants.

(*To be continued.*)

SOCIETY OF PUBLIC ANALYSTS.

ORDINARY MEETING.

Held at the Chemical Society's Rooms, Burlington House, on Wednesday, 1st October, 1924

Mr. G. Rudd Thompson, President, in the chair.

Certificates were read for the first time in favour of:—

Messrs. Arthur Cecil Brooks, A.R.C.Sc.I., A.I.C.; William Donovan, M.Sc. (New Zealand); Albert George Flower, B.Sc. (Lond.); Clifford Marshall Norman, B.Sc. (Lond.), A.R.C.S., F.I.C.; Charles Edward Sage, F.I.C.; Percy Frank Spendlove, B.Sc., A.R.C.S., A.I.C.; Charles William Spiers, M.Sc. (Bristol), A.I.C.; Leslie Herbert Trace, A.I.C., B.Sc. (Lond.); James Rawson Walmsley, A.M.S.T., F.I.C.

Certificates were read for the second time in favour of:—

Messrs. Johan Ernst Nyrop, Cand. Polyt. (Copenhagen University); Clifford Padgett Thorpe, B.Sc. (Manch.)

The following were elected Members of the Society:—

Messrs. George William Clough, D.Sc. (Birm.); James Porter Shenton, F.I.C.; William Stanley Wood.

The following papers were read:—

"The Determination of Coconut Oil and Butter Fat in Margarine," by G. D. Elsdon, B.Sc., F.I.C., and Percy Smith.

"A Preliminary Note on the Composition of the Fat of Goat's Butter," by F. Knowles, and J. C. Urquhart, B.Sc., A.I.C.

"The Quantitative Estimation of the Degree of Hydrolysis of Gallotannin by Tannase," by Miss W. N. Nicholson, B.Sc., and D. Rhind, B.Sc.

"The Pemberton-Neumann Method for the Estimation of Phosphorous," by Miss M. B. Richards, and W. Godden, B.Sc., A.R.C.S., F.I.C.

"Application of 'Formol Titration' to the Kjeldahl Method of Estimating Nitrogen," by W. S. Shaw, M.Sc., A.I.C.

The Determination of Coconut Oil and Butter Fat in Margarine, by G. D. ELSDON, B.Sc., F.I.C., and PERCY SMITH.

The Authors discuss the methods which have been suggested for calculating the percentages of butter and coconut oil present in margarine from a consideration of the Reichert-Polenske-Kirschner process. They attempt to show that a certain amount of uncertainty exists in these calculations and, from analyses of a large numbe of mixtures of known composition they attempt to introduce some improvement. The Blichfeldt process is discussed and the opinion given that this has no particular advantage over the processes now generally in use—a modification of this process suggested by the authors is found to be inferior to the Kirschner process though somewhat more rapid.

A Preliminary Note on the Composition of the Fat of Goat's Butter, by F. KNOWLES, and J. C. URQUHART, B.Sc., A.I.C.

Owing to the increasing number of herds of goats in the country and consequent increase in sale of butter obtained from this source, the authors raise the important point whether or not it is legal for this product to be sold as "butter." Analyses are given of samples of the fat or goats' butters where the usual conventional methods were employed. Particular attention is directed to the Polenske value which varies from 4.9 and 8.7 and which if interpreted in the light of the usual standards for cows' butter, would erroneously be assumed to indicate adulteration.

The Quantitative Estimation of the Degree of Hydrolysis of Gallotannin by Tannase, by MISS W. N. NICHOLSON, B.Sc., and D. RHIND, B.Sc.

Tannase disintegrates gallotannin, gallic acid being produced. The activity of tannase can therefore be measured by estimating the unchanged gallotannin. Such a method has been devised by Rhind and Smith (*Biochem. J.* 1922, *15*, 1). It can also, however, be measured by estimating the amount of gallic acid produced by the enzyme. A method for the estimation of gallic acid produced by tannase has been described by Freudenberg and Vollbrecht (*Zeitschr. physiol. Chemie*, 1921, *116*, 227). In this method the gallic acid formed by the action of tannase on gallotannin or methyl gallate is estimated by titration with sodium hydroxide, litmus paper being used as an indicator. It is assumed by Freudenberg and Vollbrecht that, under the condition

chosen by them, only the carboxyl group in the gallic acid reacts with sodium hydroxide. This method has now been tested and has been found not to be reliable. Concordant results, however, have been obtained by using a slight modification of Mitchell's colorimetric method for the estimation of small quantities of gallic acid (*Analyst*, 1923, XLVII. 2). This method has been in constant use during the last eighteen months in connection with the work of tannase and has been found to give ogod results.

The Pemberton-Neumann Method for the Estimition of Phosphorous, by Miss M. B. RICHARDS and W. GODDEN, B.Sc., A.R.C.S., F.I.C.

The chief sources of error in this estimation are (1) absorption of CO_2 hy the alkali used to disolve the ammonium phosphomolybdate precipitate, and (2) the use of a wrong factor. Errors due to (1) may be eliminated by boiling with excess of acid before the final titration. (2) Instead of Neumann's factor 0.001268, the authors use the factor 0.0011365, believing that the formula of the precipitate obtained by their procedure is $(NH_4)_3$ PO_4, 12 Mo O_3. The use of this new factor, combined with the method of precipitation and washing detailed in the paper, gives results in close agreement with those obtained by gravimetric analysis.

Application of 'Formol Titration' to the Kjoldahl Method of Estimating Nitrogen, by W. S. SHAW, M.Sc., A.I.C.

With a view to eliminating distillation tbe formol titration method was adapted to the estimation of nitrogen after the usual digestion with satisfactory results. The colourless solution is diluted and boiled to expel sulphur dioxide, neutralised and left slightly acid, and made up to 250 c.c. Twenty five c.c. of the solution are rendered alkaline with N. sodium hydroxide solution, reacidified with 0.1 N. sulphuric acid, boiled, cooled rapidly, and titrated with 0.1 N sodium hydroxide solution with phenolpthalein as indicator. Five c.c. of formaldehyde solution (commercial formalin of determined acidity) are added, the mixture allowed to stand for a few minutes, and the acidity titrated with 0.1 or 0.2 N. sodium hydroxide solution. The acidity due to the formaldehyde solution is corrected for, and the nitrogen calculated.

THE OPTICAL SOCIETY.

The first meeting of the Session 1924-25 will be held at The Imperial College, Imperial Institute Road, South Kensington, at 7.30 p.m. on Thursday, 9th October, 1924.

The following papers will be presented and discussed:—

"Some problems in the theory of optical diffraction," by E. T. HANSON, B.A.

"The annealing and re-annealing of glass," by W. M. HAMPTON, B.Sc., A.I.C.

A limited number of advanced proofs of these papers will be available before the meeting. Copies may be had on application to the Hon. (Papers) Secretary, at 50, Bedford Square, W.C.1.

Fellows and Members are invited to exhibit or describe, at any of the ordinary meetings, novel instruments or new types of apparatus likely to be of interest to the Society.

INSTITUTE OF MINING ENGINEERS

PRESIDENTAL ADDRESS.

THE VALUES FOR WHICH THE INSTITUTION STANDS.

By John Scott Haldane, M.D., F.R.S.

When Sir John Cadman informed me that Members of the Council wished me to become your next President, I was very greatly surprised. Although many years ago you definitely took me into your community by electing me an Honorary Member, the possibility of your conferring such an honour on me as making me your President had never entered my mind, and I was well aware of my lack of some of the main qualifications for the duties. As, however, the Council, in spite of this, lack, decided to nominate me, I wish to express my deep appreciation of the personal honour it has done me, and to say that I shall do my very best to follow along the pathway of the distinguished men who have preceded me.

It is now nearly thirty years since I first, in conjunction with our honoured Past-President, Sir William Atkinson, read a paper before this Institution, and began to come into close contact with the mining engineers and others belonging to the mining industry of my country. During these thirty years the contact has been a constantly widening one, leading to many close personal friendships, and, on my part,

to a better knowledge and appreciation of my own countrymen. On the scientific side it has taught me a great deal that I should never have learn from mere laboratory work.

Though I am not a mining engineer, co-operation with mining engineers has enabled me to realize the work they are doing; and perhaps the mere fact of my work being mainly in pure science, a different class of work, makes it easier for me to appreciate certain outstanding things which are embodied in the work of this Institution, and which are, and I hope always will be, characeristic of the practical aims and ideals of British mining engineers. I propose, therefore, to take as the subject of this address "The Values for which the Institution Stands."

When we look back over the volumes of *Transactions* of this Institution and the district Institutes of which it is the union, we realize the great variety of the subjects discussed at meetings, and the influence these discussions have exerted in every direction on mining practice. Our *Transactions* are, however, distinguished from those of other professional associations by the fact that questions concerning the safety and health of those engaged in the industry we represent bulk very largely in them. The reason for this is that in mining work dangers of one sort or another are constantly at hand. It is only through accurate knowledge, skill, and constant care for one another's safety, that those engaged in mining can keep the dangers at bay. At one time coal-mining in Great Britain was a relatively dangerous occupation as measured by the death-rate. It is now, and has been for many years, one of the occupations in which the death-rate is relatively low. Low as the average death-rate among occupied men in this country has, thanks to advancing civilization, become, the death-rate among coal-miners is still lower, in spite of all the potential dangers of mining work. This is the result of the knowledge, skill, and traditions of good workmanship and mutual loyalty, which have been built up during many generations. We can look back with pride to the history of British coal-mining, and look forward with corresponding confidence to continued progress in the future.

Apart from the great trade depression which is the natural result of the enormous destruction of capial during the war, the most serious existing troubles for mining engineers are those connected with what are known as "labour" questions; and it is partly the fact that has led me to choose my subject. Mining engineers have to face labour troubles along with many other troubles; but perhaps the labour troubles raise the deepest questions. This Institution stands for the interests and values which the coal-mining engineers of this country have at heart. We are apt to take the nature of these interess and values for graned; but I think that if we try to define them more clearly, this may be useful in relation to a number of problems, and particularly labour problems.

(*To be continued.*)

£20,000 LEGACY FOR LEICESTER COLLEGE.

Mr. Harry Simpson Gee, J.P., of Knighton Firth, Leicester and Eastbourne, left a fortune of £659,699, and bequeathed a legacy of £20,000 to the endowment fund of the Leicester, Leicestershire and Rutland College.

INSULIN IN TABLOID FORM.

Hitherto obtainable only as a fluid, insulin can now be obtained in compressed or tabloid form. It is put up in this form by Messrs. Buroughs, Wellcome & Co., who have for many years supplied specialities in tabloid form.

LONDON UNIVERSITY LECTURES FOR THE PUBLIC.

For a nominal fee members of the public can attend the lectures at University College, London, during the 1924-25 session. The lectures will cover a wide range of subjects by well-known scientific men.

During the Michaelmas Term this year the public lectures at King's College (London) will include the following:—

Department of Physiology.—A course of five lectures on Wednesdays, at 5.30 p.m., on "The Human Body and its Function," by R. J. S. McDowall, Professor of Physiology.

Faculty of Arts.—A course of 10 lectures on Tuesdays, at 5.30 p.m., illustrated by lantern slides, on "A Summary of Ancient

Art," by Dr. Percy Dearmer, Professor of Ecclesiasticol Art.

Department of History. A course of eight lectures on Thursdays, at 5.15 p.m., on " The Social and Political Ideas of Some Great Thinkers of the Renaissance and Reformation"—(1) " The Renaissance and the Reformation," by Dr. Ernest Barker, Principal of King's College; (2) " Nicolas of Cusa," by Dr. E. F. Jacob, Fellow of All Souls College, Oxford; (3) " Sir John Fortescue," by Miss A. E. Levett, M.A., Lecturer in History, King's College; (4) " Nicolo Machiavelli," by Dr. F. J. C. Hearnshaw, Professor of Medieval History; (5) " Sir Thomas More," by Dr. A. W. Reed, Reader in English; (6) " Disiderius Erasmus," by Professor J. A. K. Thomson, Professor of Classics; (7) "Martin Luther," by Professor J. W. Allen, Professor of History at Bedford College; (8) " John Calvin," by the Rev. W. R. Matthews, Dean of King's College.

Department of English. A course of four lectures on Mondays, at 5.30 p.m., by E. W. Scripture, Ph.D., M.D., M.A., Lecturer in Phonetics at King's Coll. The subjects include:—" Researches on Speech and Song " and " Prose and Verse analysed by the Newer Methods."

Department of Spanish Studies. Two public lectures on Thursdays, at 5.30 p.m., on " Peru, Old and New," by Señor Oscar Victor Salomón, Consul-General for Peru.

School of Slavonic Studies. A course of ten public lectures on Mondays, at 5.30 p.m., on " Austria-Hungary, 1867-1918," by R. W. Seton-Watson, D.Litt., Masaryk Professor of Central European History. A course of nine public lectures on Tuesdays, at 5.30 p.m., on " Contemporary Russia from 1861," by Sir Bernard Pares, K.B.E., M.A., Professor of Russian. A course of nine public lectures on Thursdays, at 5.30 p.m., on " The Russian Novel from Turgenev to Chekhov," by Prince D. Svyatopolk Mirsky, Lecturer in Russian Literature.

Department of Philosophy. A course of six public lectures on Tuesdays, at 5.30 p.m., on " The Philosophy of Bergson: Its Relation to Past Systems and to Present Science," by Professor H. Wildon Carr, D.Litt., Professor of Philosophy.

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

21764—Kennedy, A. M. — Methods of making arsecnical salts. Sept. 13.

21751—Naugatuck Chemical Co.—Manufacture of styrol etc. Sept. 15.

Specifications Published This Week.

221256—Grasselli Chemical Co.—Process for the manufacture of concentrated acetic acid.

221264—Pouget, L. M.—Apparatus for use in making extracts, infusions, decoctions, and the like.

202316—Gaillard, E. A. — Piston pumps suitable for acids and other liquids.

Abstract Published This Week.

220011—Alumina.—Amber Size & Chemical Co., Ltd., 61, St. Mary Axe, London.

Alumina: alkali and alkaline earth silicates; double silicates; alkali metal compounds, obtaining from complex silicates. Aluminium hydroxide is obtained by heating aluminium silicates such as china clay with alkalies or alkaline earths or their carbonates in presence of water in a closed vessel at 3-4 atmospheres pressure or in absence of water to a like temperature. Alternatively the silicate is heated with alkalies or alkaline earths or their carbonates in presence of water to a boiling temperature without pressure so as to obtain a double silicate, and then this is heated with more alkali or alkaline earth or a carbonate thereof in a closed vessel as described above to obtain alumina and an alkali or alkaline earth silicate.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

Publisher's Announcements.

The following Books can be obtained from Rea & Inchbould, Merton House, Salisbury Square, London, E.C.4.:

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THE BROMINATION OF SUBSTANCES CONTAINING A THIAZOLE RING. PART III. THE STRUCTURE OF *THE BROM BENZOTHIAZOLES*, I PHENYL BENZOTHIAZOLE TETRABROMIDE AND THE DIBROMO SUBSTITUTION PRODUCT OF 1-ANILIDO-BENZOTHIAZOLE.

By R. F. HUNTER, B.Sc., A.R.C.S., F.C.S., M.S.Chim.

In the two papers which have been published on this subject, the brom benzothiazoles discussed were essentially of the type of dehydrothiotoluidine dibromide and the bromides of the dehydrothioxylidines. With regards the bromination of benzothiazoles of the type of 4′ amino 1 phenyl 5 methyl benozthiazole, the view expressed by the author in past papers is that the mechanism of dibromo addition consists in the fission of the double bond (1:2) of the fused five membered sulphur nitrogen heterocyclic ring with the addition of two bromine atoms at this position. This view is in accordance with the general properties of the brom benzothiazoles, their mode of formation, and their ready reduction. On the other hand dibromo addition of bromine is not truly general with regards the fuzed ring thiazoles, for it has been observed that 1 phenyl benzothiazole, the parent substance of dehydrothiotoluidine adds four bromine atoms to give a tetrabromo derivative on bromination in glacial acetic acid solution. At first sight this seems somewhat peculiar, since not only dehydrothiotoluidine (*Berichte*, 1899, XXII., 422) but the dehydrothioxylidines (*Berichte*, 1899, XXII., 580) form dibromo addition products when bominated in glacial acetic acid solution, and further it has been observed by the author (*Chemical News*, 1924, CXXIX., 125) that 4′ acetyl amino 1 phenyl 5 methyl benzothiazole. the acetyl derivative of dehydrothiotoluidine forms a dibromo addition product when brominated in glacial acetic acid solution.

It has been already pointed out by the author (*loc. cit*) that if the formation of brom addition products in dehydrothiotoluidine and its higher homolugues the dehydrothioxylidines consists in the fission of the double bond (1:2) of the fused heterocyclic ring of the six membered homocyclic five membered sulphur nitrogen heterocyclic ring system, it is clear that the reaction by which dehydrothiotoluidine dibromide is produced should be general and that all benzothiazoles on bromination in solutions of suitable solvents should yield brom addition products of the type of dehydrothiotoluidine di bromide which has been suggested to be 4′ amino 1 phenyl 5 methyl benzothiazole 1:2 dibromide (I) (*loc cit*).

$$CH_3C_6H_3 \lessdot \overset{S}{\underset{NBr}{}} \gtrdot CBrC_6H_4NH_2 \quad (I)$$

$$C_6H_4 \lessdot \overset{S}{\underset{N}{}} \gtrdot CC_6H_5 \quad (II)$$

With regards the bromination of benzothiazoles of the type of dehydrothiotoluidine, the addition does take place in this way, the general reactions, stability and ready reduction of the brom benzothiazoles to the corresponding benzothiazoles by means of sulphurous acid being in accordance with a structure in which a bromine atom is directly linked to a ring nitrogen atom. As has already been pointed out in past papers, the formulation above in which a bromine atom is directly linked to a ring nitrogen atom need call for no particular comment when it is recalled that the azo linkage in phenyl diazonium bromide adds two bromide atoms to give a derivative from which an azoimide derivative can be obtained by the action of ammonia. With regards the

NOTICE OF REMOVAL.

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bromination of derivatives of dehydrothiotoluidine, it will be recalled that a number of derivatives of 4′ amino 1 phenyl 5 methyl benzothiazole prepared during the series of researches carried out by the author on the reactions of the amino group in 4′ amino 1 phenyl 5 methyl benzothiazole (*Chemical News*, 1924, CXXVIII., 34, 54, 65, 87, 103, 131, 260, 278, 414, and this vol., 37 and 77) were brominanted in alcoholic or glacial acetic acid solutions, unfortunately, however, only very small quantities of the original thiazoles were used and it was not possible to make an exhaustive study of the bromo compounds isolated; nevertheless it was shown (*Chemical News*, 1924, CXXIX., 127) *that all the benzothiazoles examined* formed brom addition products, amongst which we might mention, the brom addition products of acetyldehydrothiotoluidine, benzoyldehydrothiotoluidine, benzoyldehydrothiotoluidine, 4′ benzal amino 1 phenyl 5 methyl benzothiazole (*Chemical News*, 1924, CXXVIII., 8, 18, 147 and CXXIX., 127), the quinoline of dehydrothiotoluidine, the nitro derivative of dehydrothiotoluidine, the condensation product of dehydrothototoluidine and sulphur chloride, the condensation product of 4′ amino 1 phenyl 5 methyl benzothiazole and acetaldehyde, and 1 phenyl 5 methyl benzothiazole 4′ azo β naphthol, dehydrothiotoluidine sulphonate azo and β napthols (*Chemical News*, this *vol*. 37) *and the thio urea of dehydrothio*toluidine (*loc cit*). The bromination in all these substances has been assumed to consist of the fission of the double nitrogen carbon bond of the fused heterocyclic ring with addition of bromine at the position (1:2).

With regards the comparison of the perbromide of phenyldiazonium bromide and dehydrothiotoluidine dibromide, it must be recalled that the nitrogen atom in the latter is involved in a five membered ring and consequently the strain, induced by the direct addition to the third nitrogen valency in the latter would be expected to be less than tha in the former.

If the phenomenon of dibromo addition in the benzothiazoles of the type of dehydrothiotoluidine and its higher homologues the dehydrothioxylidines consists in the fission of the double bond (1:2), this assumes that *the double bond between the nitrogen and* carbon atoms of the fused heterocyclic ring is ethylenic in character, the instantaneous formation of brom addition products on bringing solutions of benzothiazole into contact with bromine is in accordance with this. The unsaturated double bonded formula for benzothiazoles can however only represent one phase of the bicycle benzothiazole system, for in view of the intra annual tautomeric nature of benzene and the postulated intra annual tautomerism of thiophene, it must be assumed that the thiazole ring itself is a mobile dynamic system exhibiting intra annular tautomerism, although which form this tautomerism will take and what exactly are the phases of the thiazole ring it is at present impossible to say; but in any case from the formation of brom addition products it must be assumed that one phase is that represented by the conventional for*mula for the benzothiazoles*. If one has in solution an equilibrated tautomeris system in the case of the benzothiazoles, it is clear that on bromination, the unsaturated double bonded form will react at once with bromine to form the brom addition product, this will however shift the equilibrium with the result that more of the benzothiazole is converted into the double bonded phase, and with further addition of halogen this will be converted into the addition product, the result being that the whole of the benzothiazole ultimately becomes converted into the brom addition product, the formation of the latter taking place via the unsaturated double bonded form. The more unsaturated character of the double bond in the fused *thiazole ring as compared with the mobile* double linkages in the benzene structure does not call for comment when it is recalled that the thiazole ring is considerably less aromatic in character than the benzene ring. This is exemplified by the acid hydrolysis of 1 chlorobenzothiazole to 1 hydroxy benzothiazole, and the conversion of 1 chloro zenzothiazole into 1 ethoxy benzothiazole.

It would appear then that dibromo addition in benzothiazoles of the type of 4′ amino 1 phenyl 5 methyl benzothiazole, 4′ acetylamino 1 phenyl 5 methyl benzothiazole and the dehydrothioxylidines takes place by the fission of the double hond in the fused thiazole ring, which must be to certain extent static.

On the other hand the matter is not so simple, for it will be recalled that Bogert and Abrahamson (*Jour. Amer. Chem. Soc.*, 1922, XLIV., 826) found that 1 phenyl ben*zothiazole (II.) when brominated in glacial* acetic acid forms a tetrabromo addition product. The only explanation of this would appear that the double bond of the fused thiazole ring first undergoes fission with

bromine addition in the normal manner with the addition of two bromine atoms, and the ring sulphur atom of the fused heterocyclic ring then passes from the divalent to the tetravalent state by adding two bromine atoms to give the thiazonium structure (III.).

$$C_6H_4 < {SBr_2 \atop NBr} > CBrC_6H_5$$

III.

$$C_6H_4 < {SBr_2 \atop NBr_2} > C\ C_6H_5$$

IV.

Or one can assume that not only does the addition consist in the conversion of the ring sulphur atom into the tetravalent state, but also of the conversion of the trivalent ring nitrogen atom into the pentavalent state by the direct addition of two bromine atoms, this is an alternative explanation, the tetrabrom addition product being given the formula (IV.). The sole objection to this is the fact that the structure (IV.) contains two bromine atoms directly linked to a nitrogen atom, and recalling the behaviour of nitrogen tribromide, one would expect such a compound to exhibit explosive properties, *whilst the tetrabromo derivative* of 1 phenyl benzothiazole although it slowly loses bromine at ordinary temperatures, is a relatively stable substance, being obtained in orange red crystals of definite melting point which on heating with dilute acetic acid pass into 5 bromo benzothiazole, bromine and hydrogen bromide being eliminated in the process. The fact that 1 phenyl benzothiazole tetrabromide on heating with water forms a monobromo substitution product whilst 1 phenylaminobenzothiazole tetrabromide on heating with dilute alkali forms a dibromo substitution product, is rather remarkable.

The formation of addition products from the benzothiazoles is not confined solely to bromine, for it will be recalled that Bogert and Abrahamson (*Jour. Amer. Chem. Soc.*, 1922, XLIV., 826) obtained a di iodo addition product of 1 phenyl benzothiazole. This is of course fully in accordance with the view expressed by the author in this and past papers, that the diaddition is concerned with the nitrogen atom of the fused thiazole ring whilst tetra addition of bromine is concerned with both the ring nitrogen and sulphur atoms of the thiazole ring, for the lesser affinity of iodine for sulphur as compared with bromine is well known. It will also be recalled with regards this point that the author (*loc cit*) tested a solution of dehydrothiotoluidine dibromide in glacial acetic acid for halogen ion with negative results, and if the two bromine atoms in dehydrothiotoluidine dibromide were directly attached to a tetravalent ring sulphur atom, it is obvious that the brom compound would be a thiazonium compound and therefore expected to be capable of ionisation. It is true that in view of the dielectric constant of glacial acetic acid, the latter is not a particularly good ionising solvent, yet nevertheless, it is to be expected that if dehydrothiotoluidine possessed a thiazonium structure that the halogen ion in solutions of dehydrothiotoluidine dibromide would be capable of detection by means of solutions of silver salts. This of course is in accordance with the view that the dibromo addition in dehydrothiotoluidine is not connected with the ring sulphur atom.

It will be recalled, in connection with another series of investigations of the author on the stability of the brom benzothiazoles (*Chemical News*, 1924, CXXVIII., 163) that the suggestion was put forward in view of the remarkable fine fluorescence of *dehydrothiotoluidine in alcoholic solutions and certain of its derivatives in solutions* when exposed to ultra violet light (*Chemical News*, 1923, CXXVII., 385) that dehydrothiotoluidine in the form of an alcoholic solution under the action of ultra violet light, may consist of a tautomeric system, consisting of three phases, the normal form of dehyrothiotoluidine having the conventional formula, another double bonded phase having a double bonded sulphur atom, and these two dynamic phases in equilibrium and capable of interconversion by means of an intermediare bridged phase in which the bridge is between the sulphur and nitrogen atoms of the fused five membered sulphur nitrogen heterocyclic ring. It was shown that if such a system was treated with bromine that the brom addition products first formed would on account of their instability pass almost at once into the normal form of dehydrothiotoluidine dibromide, it was in connection with this suggestion that the possible ionisation of dehydrothiotoluidine dibromide was examined. The postulation of dehydrothiotoluidine in the form of solutions as being a three phase

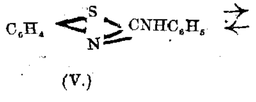
intra annular tautomeric system of the type suggested would of course account for the remarkable fine fluorescence of certain compounds of the series, but the suggestion involves the assumption of trivalent sulphur in the labile form which appears unlikely, nevertheless it is firmly believed that dehydrothiotoluidine and the benzothiazoles in general exhibit tautomerism involving the motion of valencies across the five membered heterocyclic ring. It must of course be assumed that the normal and stable form of the benzothiazoles is that indicated by the conventional formula which is based essentially on the experience of Hofmann on the fission and synthesis of 1 phenyl benzothiazole (*Berichte*, 1879, XII., 2359) and the general synthesis and reactions of the fused ring thiazole series. On the other hand it is hard to see why the benzothiazoles should form brom addition products instantaneously on being brought into contact with solutions of the halogen, whilst thiophene, as is well known, is remarkably unreactive in its chemical properties and simulates benzene in general reactions.

Further, it is hard to understand why 1 phenyl benzthiazole forms a tetrabromo addition product (III.) by the fission of the bond (1:2) with addition of two bromine atoms, and addition of two bromine atoms at the ring sulphur atom, whilst 4′ Amino 1 phenyl 5 methyl benzothiazole and 4′ Acetylamino 1 phenyl 5 methyl benzothiazole only add two bromine atoms to give stable dibromo addition products. It is far from clear why the ring sulphur atom (7) in dehydrothiotoluidine and its higher homologues is more saturated and therefore unreactive towards bromine while in 1 phenyl benzothiazole it is reactive and readily adds two bromine atoms. Still more remarkable is the fact that 1 amino benzothiazole only adds two bromine atoms when a suspension of its hydrobromic acid salt is brominated in chloroform, whilst 1 phenylaminobenzothiazole is obtained in the form of a tetrabromide which passed on reduction into 1 phenylaminobenzothiazole when diphenylthiourea is brominated in chloroform solution. The remarkable instability of acetyl dehydrothiotoluidine dibromide is another subject calling for comment, for the brom addition product of the benzoyl and benzal derivatives of dehydrothiotoluidine as prepared by the author have been found to be stable substances, whilst 4′ acetylamino 1 phenyl 5 methyl benzothiazole dibromide (*Chemical News*, 1924, CXXIX., 125) loses bromine on keeping at ordinary temperatures and gives very poor figures on analysis for bromine on keeping for two or three days. The stability of dehydrothiotoluidine dibromide towards hydrolysing agents (*loc cit*) also appears peculiar when it is recalled that the acetyl bromo compound splits off bromine on merely warming with water.

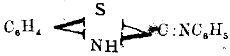
In view of these facts, it was considered in view of the importance of the researches on the benzothiazoles published in this journal, of interest to prepare and examine the tetrabromide of 1 phenyl benzothiazole. The 1 phenyl benzothiazole was obtained by the thionation of benzal aniline obtained by condensing equimolecular proportions of aniline and benzaldehyde at a temperature of 140° for several hours. The 1 phenyl benzothiazole being brominated in glacial acetic acid according to the directions of Bogert and Abrahamson. The compound was found to pass into 5 bromo 1 phenyl benzothiazole by merely diluting the solution of brom thiazole and warming as recorded by these investigators.

At this point it is desired to place on record an observation made with regards quite another investigation. It will be recalled that Hugershoff (*Berichte*, 1903 XXXVII., 3120) observed that when the tetrabromide of 1 anilido benzothiazole is treated with dilute alkalis it passes into a dibromo substitution product of 1 anilidobenzothiazole. Hugershoff did not however assign a structure to the dibromo substitution product, nor did he make any suggestions as to its probable constitution.

From this synthesis of 1 phenylamino benzothiazole by the action of aniline on 1 chlorobenzothiazole, 1 phenylamino benzothiazole should clearly have the constitution (V.), while on the grounds of the Hugershoff synthesis from diphenylthiourea by bromination of the latter in chloroform solution and subsequent reduction of the brom addition product, the constitution (VI.) is equally justifiable, and it would seem probable that 1 phenylaminobenzothiazole betrays tautomerism of the type,

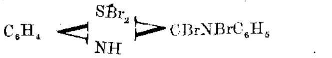


(V.)

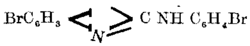


(VI.)

that is involving the motion of the mobile hydrogen atom, in the same way as isatin betrays lactim-lalctam tautomerism. If this is the case, the form (VI.) will add bromine to give the bromo compound (VII.), this on treatment with alkalis will clearly pass into a compound of the structure (VIII.), the bromine atom migrating to the para position of the phenylamino grouping to give a substitution product in the same way as the brom addition product of benzal aniline is converted into the para bromo substitution derivative. This would account for one substituted bromine atom, the most probable position for the second is in the fused six membered homocyclic ring of the bicyclic benzothiazole system, most probably in the position (5)

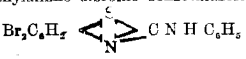


(VII.)



(VIII.)

since I phenyl benzothiazole bromide readily passes into a 5 bromo substitution product by warming with dilute acetic acid, the dibromo substitution product of Hugershoff being (VIIII.). On the other hand it appears possible that all substitution takes places in the fused benzene ring of the benzothiazole system, in which case *the dibromo substitution product would* be 1 phenylamino dibromo benzothiazole (IX.)



(IX.)

The point is clearly settled by the hydrolysis of the benzothiazole; if the compound (VIII.) is fused with potash for a few minutes, the fused thiazole ring will be ruptured with the production of a bromo aminophenyl mercaptan and the formyl derivative of parabromo aniline, which in the presence of hot potash will break down into formic acid and parabromoaniline, while on the other hand if the dibromo substitution product of Hugershoff has the constitution (IX.) it is clear that one of the hydrolytic fission products will be aniline. On fusing the dibromo substitution product of 1 phenylaminobenzothiazole, with potash, no aniline was formed, and the products did not react with hypochlorite showing the absence of even a trace of aniline, on this account it appears probable that the dibromo substitution product of 1 phenylaminobenzothiazole has one substitutent in the fused homocyclic ring of the benzothiazole system and one in the aniline residue, the constitution which would appear likely on theoretical grounds is that of 1 parabromophenylamino 5 bromo benzothiazole (VIII.), although the matter cannot be looked upon as settled. The non production of aniline as a fission product is of course distinctly against the constitution (IX.).

Experimental.

1 Phenyl benzothiazole

60 gms of aniline were mixed with theoretical equivalent of benzalehyde in a 500 cc flask and the mixture kept at 140° C for five to six hours to remove the water of condensation. The solid condensation product so obtained was mixed with 40 grms of flowers of sulphur and the flask heated in an oil bath at about 260° C for five hours. A vigorous evolution of hydrogen sulphide took place during the first stages of the reaction, but this slackened after the first three hours or so. The melt was poured while hot into a basin and allowed to cool. The melt was so obtained as a bright shining black solid. The melt when quite hard was chipped out of the basin, broken up into small pieces and finally crushed to *a fine black powder in a mortar.* The crushed melt was transferred to a litre round bottomed flask containing 300 ccs of concentrated hydrochloric acid, and the mixture refluxed on a sand bath for one to two hours. The clear brown acid extract was filtered hot through glass wool into a litre of cold water, when the phenyl benzothiazole was obtained as a pale yellow nearly white bulky precipitate. The precipitate was filtered at the pump after standing for some hours, and well washed with water and air dried. The benzothia-

ozle so obtained is pure enough for most properties. A small portion recrystallised from alcohol containing a little animal charcoal melted at 115° C as recorded. The yield was 38 gms.

1 Phenyl benzothiazole tetrabromide

3 gms of phenyl benzothiazole were dissolved in 80 ccs of glacial acetic acid and the solution cooled to room temperature in a 300 cc conical flask. 3 ccs of Bromine were then added drop by drop from a burette charged with the liquid halogen with steady shaking of the flask. The addition and shaking being carried out over a period of ten minutes or more, the flask was then allowed to stand for an hour when orange red needles of the tetrabromide deposited which were filtered, and the crystals dried first on a porous tile and then in a desiccator. The addition of bromine must be carefully regulated, or the crystals will become contaminated with a brown solid. The crystals are unstable and gradually lose bromine in contact with air. If the solution of the crystals in glacial acetic acid solution is diluted with a little distilled water and the mixture boiled till it is colourless, bromine and hydrogen bromide are evolved and the hot solution on cooling deposits white crystals of 5 bromo 1 phenyl benzothiazole which are readily recrystallised from acetic acid.

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SODIUM TUNGSTATE.

By Edgar F. Smith.

(Contribution from the John Harrison Laboratory of Chemistry—University of Pennsylvania.)

(*Continued from Page 225.*)

$4\ Na_2O\ .\ 10\ WO_3\ +\ 23\ H_2O$ requires:

H_2O	13.88%
WO_3	77.79%
Na_2O	8.33%, while the

synthetic product yielded:

H_2O	13.73%	13.64%	13.80%	13.88%
WO_3	17.55%	77.72%	77.83%	77.97%
Na_2O	8.52%	8.64%	8.37%	8.21%

At this point it may be well to remember that Marignac (Compt. rend. 55, 888; Ann. chim. phys. (3) 69, 5, (1863)) described a salt to which he assigned the formula $3\ Na_2O\ .\ 7\ WO_3\ +\ 16\ H_2O$ (or $21\ H_2O$). It differed altogether from the 5:12-salt. It was suggested that it might be a polymeric form of ordinary sodium *para*-tungstate; and there were not a few who believed it really did not exist. In the writer's experience it has frequently appeared, in the filtrates of the 5:12-salt, when these were allowed to evaporate spontaneously. It consisted of beautiful, vitreous crystals. On referring to the scheme of arrangement at the head of this communication the salt holds the third place among the soluble tungstates. From time to time samples of it were subjected to analysis. For example, one gram of material gave:

Found		*Theory*
13.70%	H_2O	13.72%
77.56%	WO_3	77.41%
8.70%	Na_2O	8.87%

One tantalizing feature of the salt is that upon resolution in water it changes very quickly to the 5:12-salt. Naturally, one wonders, after the experiences with the 5:12 and the 4:10-salts whether this 3:7-salt is not a combination of normal sodium tungstate with the meta-salt in this sense:

$$3(3\ Na_2O\ .\ 7\ WO_3\ +\ 16\ H_2O) \quad 5(Na_2O\ .\ WO_3\ +\ 2\ H_2O)\ +\ 4(Na_2O\ .\ 4\ WO_3\ +\ 9.5\ H_2O)\ .$$

Accordingly 5 grams of the salt were dissolved in a litre of water. The solution was boiled for some time, then cooled to 80° C., when 75 cc. of hydrochloric acid (sp. gr. 1.185) were added. The separated tungstic acid, representing the normal acid in the 3:7-salt, weighed 0.9051 gram instead of 0.9215 gram (calculated). In the filtrate there was isolated the *meta* acid which weighed 2.98 grams, instead of 2.95 grams (theory). The ratio, then, in which the 1:1-salt and the 1:4-salt existed in this 3:7-salt, was as 1:2.83; and, on bringing together, in this ratio, pure normal and pure meta-sodium tungstates, beautiful crystals of the *synthetic* 3:7-salt appeared. On analysis one gram gave:

Found		*Theory*
13.76%	H_2O	13.72%
77.60%	WO_3	77.41%
8.64%	Na_2O	8.87%
100.00%		100.00%

Another fact follows from this synthesis, viz. the para-tungstates possess the 5:12-salt formula. They contain

0.8600 gram WO_3 belonging to the normal salt present in them,

and 3.0000 grams WO_3 belonging to their meta-salt, whereas, from the observations just given the 3:7-salt holds:

0.9215 gram WO_3 belonging to its meta constituent.

Similar results came on hydrolyzing further portions of the synthesized 3:7-salt.

A glance at the arrangement of the soluble tungstates, shown above, plainly argues for 1:1 and 1:4-salts as the real fundamental bodies among the soluble tungstates. The intervening compounds are combinations of the members 1 and 7—nothing more. Three of them—the members 3, 4 and 5—have been synthesized and hydrolyzed, thus revealing again their constitution.

What can be said for the remaining two—the members 2 and 6? Lefort announced them (*Ann. chim. phys.* (8) *9*, 97 (1876)). No other chemist has succeeded in preparing them by his plan. (Kautschew, J. Russ. phys. chem. Ges. *48*, 692; Gonzalez, J. prakt. Ch. *36* (1887), 47; J. prakt. Ch. N.F. *27*, 84.) Adopting the scheme pursued in the synthesis of the 3:7, 5:12 and 4:10-salts, it is quite clear that 2 molecules of the 1:1 and 1 molecule of the 1:4-salts should units to 3 molecules of the 1:2-salt:

$$2\ (Na_2O\ .\ WO_3) + Na_2O\ .\ 4\ WO_3 \quad 3\ (Na_2O\ .\ 2\ WO_3)$$

and in like manner 1 molecule of the 1:1 and 2 molecules of the 1.4-salts should give rise to 3 molecules of the 1:3-salt:

$$Na_2O\ .\ WO_3 + 2\ (Na_2O\ .\ 4\ WO_3) \quad 3\ Na_2O\ .\ 3\ WO_3)$$

With pure normal and pure meta sodium salts it was set about to realize these syntheses. Not once was there the slightest evidence that the 1:2-salt was produced. With the 1:3-salt, the experience was as follows. When the salts (1:1 and 1.4) were brought together in the ratio of the preceding equation, crystals appeared after the solution had stood overnight. These were removed, washed with small quantities of ice water, then dried between hibulous paper and analyzed. They gave the percentage requirements of the 4:10-salt. The liquid from these crystals was permitted to evaporate spontaneously. The material which separated after several days had the 1:4-salt clinging to it, so it was washed quickly with ice water, in small portions, dried between paper and analyzed.

Analysis.

H_2O	13.63%	13.29%	13.81%	13.69%
WO_3	78.92%	78.85%	78.57%	78.58%
Na_2O	7.45%	7.86%	7.62%	7.73%

The sodium oxide and tungsten trioxide here approximate the ratio 1:3 and the results give rise to a formula:

$Na_2O\ .\ 3\ WO_3 + 7\ H_2O$, which would require

14.25%	H_2O
78.62%	WO_3
7.01%	Na_2O

There is but a suspicion in these results that the 1:3-salt was actually formed, not, however, in a pure state. When it was sought to get it pure by recrystallization with water, the product invariably proved to be the 1:4-salt. Hence, the old enemy—hydrolysis—was again at work. And this is also unquestionably the reason that in striving to prepare the 1:2-derivative, the constant result was the 5:-12 salt. In this tendency of the 1:3-salt to hydrolyze into the 4:10-salt, there is repeated the conduct of the 3:7-salt, which, on solution in water, passes promptly into the 5:12-salt.

(To be Continued).

GENERAL NOTES:

OIL VERSUS COAL AS FUEL.

The Civil Lord of the Admiralty, Mr. Frank Hodges, M.P., delivered an interesting address at the Wigan Mining College on October 4th. He said that they now imported large quantities of oil fuel into this country, and it was making itself felt already upon the coal trade. Last year they imported 5,000,000 tons of oil of all kinds, at an approximate cost of £45,000,000, more than half of which came from the United States and Mexico. It was the change over from coal to oil as the fuel for their Fleet and mercantile marine where they saw the best example of the struggle between coal and oil as fuel. Lloyd's register showed to what extent oil had been adopted for tonnage built since the war. For 1918-19 the oil-using tonnage was about 33 per cent. of the whole, for 1919-20 nearly 50 per cent.,

for 1920-21 60 per cent., for 1921-22 64 per cent., and for 1922-23 59 per cent. "Unless Great Britain keeps pace with the rest of the world in the struggle to get power at the cheapest possible cost," said Mr. Hodges, "she can therefore bid good-bye to all thought of continued commercial supremacy. Her coal trade will go from bad to worse and the prospects of her children will be far from rosy."

To-day they raised 260,000,000 tons of coal per annum, of which approximately 65,000,000 tons were sold abroad and to ocean going and coasting steamers, while 195,000,000 tons were consumed at home. Of this, in normal times, about 40,000,000 tons were carbonized, 50 per cent. in gas works and 50 per cent. in coke ovens, leav- 155,000,000 tons which were burnt as raw coal. This was a crude and wasteful proceeding, since it was now definitely proved that coal could be treated by scientific methods of carbonization, quite different from the existing high temperature methods of the gas works and the coke oven, so as to obtain large quantities of high grade gas, motor spirit and other liquid fuel, especially for Diesel engines; sulphate of ammonia for the cultivation of the soil, and residual smokeless fuel, which was infinitely more efficient than our raw coal. It was now being recognized everywhere that to burn raw coal at all was a crime, and in no country in the world did this apply more forcibly than in Great Britain, since they had no petroleum oil, only about one million horse power of potential inland water power, and did not make anything like adequate use of the soil for food production.

To-day they were said to be paying to foreign countries abroad something like £45,000,000 per annum for motor spirit and oil fuels generally, and about 200,000,000 gallons of motor spirit aone was imported every year. From the point of view of Great Britain, the position was both serious financially and dangerous from the point of view of national safety. "We are being bled by foreign countries in the shape of high prices of motor spirit and petroleum to such an extent that the whole motor industry of Great Britain is crippled and our transport charges are far too high," said Mr. Hodges. "Then from a military and naval point of view we are dependent almost entirely on foreign countries for petrol for aircraft and motor transport, including artillery and tanks, and for liquid fuel for the Navy. Our communications with sources of supply thousands of miles away can be cut off by submarines and aircraft, and steps against this necessitates a formidable outlay of men and material. Still more serious—and this is not yet realised even by most engineers—is that the condensing steam-engine and the turbine are doomed, and almost within the next few years most of the power of the world will be generated by the internal combustion, heavy oil, Diesel or semi-Diesel, engine."

Modern scientific methods of carbonization now perfected, Mr. Hodges pointed out, would give on the average from one ton of coal, three gallons of motor spirit, 18 gallons of crude dry pariffinoid oils, of which at least 50 per cent. was available for Diesel oil, and, say, two gallons as lubricating oil, and 30lb. of sulphate of ammonia, together with 14 cwt., or 70 per cent. of the weight of the coal, of residual smokeless free-burning fuel. This meant that if they treated the 145,000,000 tons of raw coal on these lines, they should have available every year 435,000,000 gallons of motor spirit or twice their present consumption 62,000,000 barrels of crude oil, of which over 30,000,000 barrels would be Diesel oil, with over 6,500,000 gallons of lubricating oil, and 1,900,000 tons of sulphate of ammonia for the cultivation of the soil, and 101,500,000 tons of smokeless fuel. It was certain that by the extraction of the valuable products of coal by carbonization, and the raising of steam by a mixed supply of surplus gas, pulverized smokeless fuel or raw grade coal could be used, not in small generating stations dotted throughout the country, but at bulk power-producing centres at the coalfields. Cheap electric supply in bulk would result in the rapid and profitable electrification of suburban railway services, even if main line locomotives were for a time run with smokeless fuel.

NEW BRITISH CHEMICAL STANDARD STEEL.

Messrs. Ridsdale & Co. announce the issue of British Chemical Standard Carbon Steel "E" (B.O.H.) having the following standardised figures:—

Carbon	0.114%
Manganese	.492%

This material has been specially prepared

to meet the need for widely recognised carbon (colorimetric) standard above 0.10%, which is near to the maximum usually desired in tin-plate manufacture. It has the additional convenience of being a low manganese standard, so that those who prefer to determine the carbon (colour) and manganese from the same porton of sample may do so.

As usual, the analysis has been conducted by a number of Independent Analysts, Works' Chemists, etc. (including the Bureau of Standards, Washington, U.S.A.) representing different interests.

Bottles of standard turnings may be obtained from Headquarters, 3, Wilson Street, Middlesbrough, at a fee estimated to be sufficient to cover the cost of preparation. Three sizes are now provided, viz., 500 grammes, 100 grammes, and 50 grammes.

A certificate giving the names of the analysts co-operating, the types of methods used (including numerous notes thereon) and a detailed list of individual analyses, will be supplied with each bottle.

LIGNITE UTILISATION IN CANADA.

The High Commissioner for Canada has received for the reference library a copy of the First General Report of the Lignite Utilisation Board of Canada, which contains some valuable papers dealing with the experiments which have been made in connection with the problem of carbonising and briquetting of Saskatchewan Limited. The Report in question could be consulted at the Office of the High Commissioner for Canada, Kinnaird House, Pall Mall East, London, S.W.1., by chemists, engineers, and others interested.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE BRITISH ASSOCIATION.

(*Continued from Page* 229.)

Although no one can set limits to the possibilities of plant breeding and plant physiology, we cannot assume that we are anywhere near this desirable achievement or that we are likely to be in our time. There will always remain the necessity for altering the environmental conditions to bring them closer to the optimum conditions for the growth of the plant. No attempt is yet made in the field to control two of the most important of the factors: the light and the temperature, though it is being tried experimentally. There is a great field for future workers here; at present plants utilise only a fraction of the radiant energy they receive. At Rothamsted attempts have been made by F. G. Gregory to measure this fraction; the difficulties are considerable, but the evidence shows that our most efficient plants lag far behind our worst motor-cars when regarded as energy transformers for human purposes. One hundred years ago the efficiency of an engine as transformer of energy was about 2 per cent.; now, as a result of scientific developments, it is more than 30 per cent. To-day the efficiency of the best field crop in England as transformers of the sun's energy is about 1 per cent. [The remaining energy being largely used up in transpiration. This figure refers to the total radiation received *by the leaf, and not to the fraction received* by the chloroplast surface. For this latter the value is much higher.]: can we hope for a similar development in the hundred years? If such an increase could be obtained an ordinary crop of wheat would be about 400 bushels per acre, and farmers would feel sorry for themselves if they obtained only 200 bushels. But we are only at the begining of the subject. Increases in plant growth amounting to some 20 or 25 per cent. have been obtained by V. H. Blackman in England under the influence of the high-tension electric discharge, which presumably acts by increasing in some way the efficiency of the plant as an energy transformer. Possibly other ways could be found. It needs only a small change in efficiency to produce a large increase in yield. Much could be learned from a study of the mass of data which could be accumulated if agricultural investigators would express their results in energy units as well as at present.

Interesting results may be expected from the attempts now being made in glasshouse culture both in Germany and at Cheshunt to increase the rate of plant growth by increasing the concentration of the carbon dioxide in the atmosphere.

CONTROL OF THE SOIL FACTORS.

The soil factors lend themselves more readily to control and much has been already achieved. Water supply was one of

the first to be dealt with. Civilisation arose in the dry regions of the earth, and as far back as 5,000 years ago irrigation was so advanced as a practical method that it came into the ordinances drawn up by the great Babylonian king Hammurabi. The chief problems at the present time are to discover effective means of economising water and to ascertain, and if possible control, the relationships between the soil, the water, and Economical use of water is necessary because it allows larger areas to be irrigated, and because water beyond a certain amount injures the soil and asphyxiate the plant roots. This part of the problem is largely one of engineering and police control. The more serious problem, perhaps the most serious confronting agricultural science to-day, is that presented by the soluble matter in the water and the soil. The terrible spectre of alkali looms ahead of every irrigation project; it may be kept under control for a longer or shorter time or it may completely wreck the scheme. Instances could be multiplied of schemes started with great expectations of results yet yielding only disappointment and loss. A volume could be filled with the tragedies of the alkali problem. Neutral salts, particularly sodium sulphate, are not harmful to plants unless their concentration exceeds a certain critical value; indeed, some of the heavy soils in dry countries, as in Egypt and the Sudan, become unworkable if washed with pure water; they remain flocculated only because some soluble salts are present. Chlorides beyond a critical concentration are more harmful to the plant, but sodium carbonate is deadly, and there is no certain way at present of overcoming its effects.

The empirical method has apparently gone as far as it can, and nothing more can be expected until some fresh opening is discovered by scientific workers.

Almost equally important is the more efficient utilisation of water in districts where the rainfall is sufficiently high to obviate the need for irrigation, but insufficiently to allow of any wastage of water. The practical work of the Utah agriculturists as exemplified by Widstoe, and the laboratory results of Keen at Rothamsted, all indicate that something can be done. It is legitimate to hope that the next great advance will come from Canada, where in the West there are admirable opportunities for studying the problem.

Inseparably bound up with water supply are the questions of cultivation and of drainage, which affect not only the water but the air supply to the roots. This former subject is now attracting considerable attention: the great need is to discover means for expressing cultivation in exact physical and engineering units. The measurements of Keen and Haines of Rothamsted, and the chemical work of A. F. Joseph, N. Comber and others on clay, and of Odén, Page, and others on humus, indicate the possibility of finding exact expressions and of affecting co-operation with the workers in the new fields of agricultural engineering.

Another soil factor which readily lends itself to some degree of control is the amount of plant nutrients present. The possibility of increasing this by means of manure has been so frequently explored in field trials that it has sometimes been regarded as almost a completed story; indeed, Rothamsted tradition affirms that Lawes himself once gave orders to have the Broadbalk field experiments discontinued because they had nothing further to tell; it was only the earnest persuasion of Gilbert that caused him to countermand the order. So far from the subject being exhausted, it still bristles with problems. The new nitrogenous fertilisers, resulting from war-time activities in nitrogen fixation; the need for reducing the cost of superphosphate; the change in character of basic slag; and the Alsatian development in potash production are producing changes in the fertiliser industry the full effects of which are not easy to foresee. Economic pressure is driving the farmer to derive the maximum benefit from his expenditure on fertilisers, lime, farmyard manure and other ameliorating agents, and is compelling a more careful study of possibilities hitherto disregarded, such as the use of magnesium salts, silicates, and sulphur as fertilisers, and, above all, a much more precise diagnosis of soil deficiencies than was thought necessary in pre-war days.

(To be continued.)

INSTITUTE OF MINING ENGINEERS

Presidental Address.

The Values for which the Institution Stands.

(Continued from Page 232.)

The capital sum in use, and at the same time at risk, in the undertakings managed by members of this Institution is enormons.

If, through inefficient management or other causes, these undertakings ceased to pay a reasonable dividend, that capital would be lost. Let us see what this would mean. Some of the undertakings might be able to struggle on for a time, leading a hand-to-mouth life, with no credit to fall back on for the cost of necessary replacements or improvements; but this could not last long. Meanwhile a great many shareholders, rich and poor, would have lost all benefit from their savings. To the poor shareholders regarded as individuals this would be a calamity; to the rich it might be a personal relief from endless cares and responsibilities which accompany the control of much wealth, but many persons dependent on that wealth for their employment would suffer. What I wish to emphasize, however, is that the country, and on a wider view other countries, too, would have lost the capital.

Capital means, not merely the power of doing wo.k, but the power of doing productive work—work which will afterwards bring a net profit. Such work is always done on credit, of which money is the token. In proportion as an undertaking ceases to pay or give evidence of paying in the future, its credit or capital disappears. This, unless it has been foreseen and provided for, means disappearance of national credit or capital. Power of giving employment over a circle of which the width cannot be estimated has disappeared, as well as taxible income for both national and local purposes. When we realize the actual responsibility to their fellow-countrymen of those whose duty it is to care for the financial soundness of the operations involved in British colliery undertakings, we see at once how great that responsibility is, and how important it is that sufficiently far-seeing men should bear it, and should not be suffered to be interfered with by ignorant persons who are commonly officious in direct proportion to their ignorance.

I think there will be general agreement that one of the values for which this Institution stands is the capital or credit of the coal-mining undertakings of this country. Every improvement in mining practice adds to that capital or prevents its disappearance, and this Institution is constantly engaged in promoting these improvements and spreading the knowledge of them among mining engineers. I think, also, however, that it will be strongly felt that the Institution stands at the same time for other values.

From its early beginnings it has certainly stood for safety and health in mining operations; and not merely because without a reasonable standard of safety and health mining work would be more expensive, but because care for the safety and health of those employed in mining is part, and a very important part, of the direct duty of a mining engineer. Such contributions as I have myself been able to make towards the work of the Institution have been concerned almost entirely with questions of safety or health. The interest with which these and other similar contributions have been received and discussed, and, indeed, the mere fact that you have asked me to be your President, though I am not otherwise concerned in mining, are sufficient evidence that safety and health stand prominent among the values for which the Institution stands.

There are, however, still other values, and of a less palpable but more comprehensive kind, embodied in the work of members of this Institution; and it is these other values that contact with the coal-mining industry of my own conntry has more particularly made me conscious of. The collieries of this country would be quite different places from what they are but for the presence in them of a comradeship capable of dominating all other considerations. I have often been present at a colliery during some time of trouble or danger; and it was this comradeship, from highest to lowest, that impressed me most. But whether or not unusual trouble is present, one seems to meet comradeship as one enters the colliery premises or steps into the cage. It is part of the atmosphere of a British pit, and real pitmen seem always to carry some of it round with them, so that the meetings of the Institution abound with it.

Comradeship is just action based on the placing of value upon the interests of neighbours. It carries with it respect, and the very highest kind of respect, for those who show it, whether they be rich or poor, known or unknown. It is comradeship that inspires, and has made, our Institution: comradeship not merely between its members, but also between them and all those engaged in the mining industry. It seems to me that among the values for which this Institution stands those which are embodied

in what may be called comradeship are the most important, and in reality embrace the rest.

As collieries have become larger and deeper, so that machinery and organization of a far more complex character have come into use, the need for scientific knowledge, technical experience, and organizing power on the part of mining engineers have constantly increased. So also has the need for seeing to the proper provision above-ground of housing and educational and other facilities for the larger number of miners who are required and their families, and to the proper training of mining engineers and colliery officials. But so also, and this perhaps needs emphasis, has the need grown for a more extended realization of the conception of comradeship or Christian charity in connexion with mining. It is not with scientific abstractions called "Labour" and "Capital" that British mining engineers have to work, but with their own fellow-countrymen, their own flesh and blood. These fellow-countrymen will give loyal and efficient service, will face any danger, will forgive imagined or real mistakes, and will take the rough with the smooth, the bad times with the good; but what they will not tolerate is being treated as if they were mere tools, to be cast aside without compunction. Neither high wages, high dividends, nor welfare schemes will satisfy them in this respect, but only discerning and sympathetic treatment, the treatment of comradeship in a common enterprise—and comradeship as existed in and between all ranks during the war, or such comradeship as is taught in the Gospels.

(To be continued.)

THE CHEMICAL SOCIETY.

Ordinary Scientific Meeting, held Thursday, October 16th, 1924, at 8 p.m. The following papers were read:—

"The Influence of Catalysts on Carbonisation," by R. Lessing and A. L. Banks.

"The Photosensitive Formation of Water from its Elements in the Presence of Chlorine," by R. G. W. Norrish and E. K. Rideal.

"Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXIV. Further experiments on the Walden Inversion," by J. Kenyon, H. Phillips and H. G. Turley.

"The Directive Influence of Substituents in the Glyoxaline Nucleus on Substitution in the Benzene Nucleus of Phenylglyoxalines—the Nitration of 2-phenylglyoxaline and its Carboxylic Acids," by F. L. Pyman and E. Stanley.

ROYAL MICROSCOPICAL SOCIETY.

The section of the Society which has been formed to deal with the Industrial Applications of the Microscope, and to assist in the development of Scientific Research in British Industries, will hold its next meeting at 20, Hanover Square, W.1, on Wednesday, 22nd October, 1924, at 7 for 7.30 p.m.

PROGRAMME.

Mr. A. Chaston Chapman, F.R.S., F.I.C., P.R.M.S., will preside. 7.30 p.m., Mr. Joseph E. Barnard, F.R.S., F.Inst.P., F.R.M.S., will give the first of a series of Lecture Demonstrations on the Elementary Principles of Microscopical Illumination. (1) Transmitted Light. 8.30 p.m., Election of Committee.

METALLURGICAL MICROSCOPY.

"Super-saturated Solid Solutions," by Dr. R. H. Greaves, D.Sc.

"New Photo-micrographic Apparatus for all Purposes," by Mr. Harold Wrighton, B.Met., F.R.M.S.

SOCIETY OF GLASS TECHNOLOGY.

A Meeting of the Society was held in the Applied Science Department, The University, Sheffield, on October 15th. The following paper was read and discussed:—

"The Present Position of the Glass Industry in North America," by Prof. W. E. S. Turner, D.Sc.

UNIVERSITY OF LONDON.

ADVANCED LECTURES IN CHEMISTRY.

Two Lectures, entitled (1) "Organic Radicals"; (2) "Theory of Oxidation Processes," will be given at King's College, London (Strand, W.C.2), by Prof. Dr. Heinrich Wieland (Professor of Chemistry in the University Freiburg) at 5.30 p.m.

on Thursday, October 16th, and Friday, October 17th, 1924.

At the first lecture the chair will be taken by Professor Samuel Smiles, F.R.S., O.B.E. (Daniell Professor of Chemistry in the University).

The lectures, which will be delivered in English, are addressed to students of the University and to others interested.

Admission free, without ticket.

JUNIOR INSTITUTION OF ENGINEERS.

On Friday, October 3rd, Prof. A. W. Bickerton, A.R.S.M., delivered a lecture entitled "Explosions, Terrestrial and Celestial."

Prof. Bickerton spoke of many of his early experiments and researches in connection with explosions of chemical compounds such as gunpowder, dynamite, and guncotton, and explained how he came to apply the principles underlying such explosions in the study of astronomy and particularly with regard to the formation of new stars, or exploding suns as he called them. He came to the conclusion, he said, that a collision between one tenth part of a pair of stars would produce a result 10,000 times as effective as a head-on collision, and all his subsequent work had supported his theory that grazing collisions between stars were responsible for the formation of most new stars with their attendant nebulae and debris. The new star, or third body, received practically all the heat generated by the collision, and consequently attained immense brilliance, though it might die out in the course of a few days. The two stars which had collided would become a pair of variables, and from an actual chart of variable stars in a small portion of the heavens, eighteen variables had been found to be close pairs.

The lecture was illustrated by a number of slides showing photographs of stars and nebulae, and also spectra of new stars with peculiar dark lines crossing each band. In connection with some of the slides, Prof. Bickerton referred to the ways in which the forces of nature are exerted and the way in which they may accumulate and give rise to spectacular displays.

CORRESPONDENCE.

THE BROMINATION OF SUBSTANCES CONTAINING A THIAZOLE RING.

The Chemical Laboratory,
Highbury New Park,
N.5.

To the Editor of the CHEMICAL NEWS.

Dear Sir,

In a recent paper communicated to this Journal on the subject of the bromination of thiazole ring (Part III.), I stated that the probable structures of the tetra bromine addition products of the benzothiazoles (with reference to 1 phenyl benzothiazole tetrabromide) was that of 1:2:7:7 tetrabromo compounds, and that this formulation appeared more probable than the one which regards tetra bromo addition as consisting of the conversion of the ring nitrogen atom from the trivalent state into the pentavelent state along with the conversion of the divalent sulphur atom of the fused thiazole ring into the tetravalent state, since the former structure contains a nitrogen atom directly linked to one bromine atom while the latter contains two bromine atoms directly linked to a nitrogen atom, and nitrogen tribromide in which the bromine atoms are directly linked to the nitrogen is explosively unstable whilst the bromo addition products of the benzothiazole series are in many cases crystalline compounds of definite melting point and are quite stable below 100 C.

This reasoning contains an obvious fallacy which has since been pointed out to me, the fallacy being that the nitrogen atom in nitrogen tribromide is in the trivalent state whilst that in the formulation of brom benzothiazoles as containing a doubly linked nitrogen atom attached to two bromine atoms, is in the pentavalent state. From which it is clear that the structure best in accordance with the facts is that containing pentavalent nitrogen. However, it is hoped to discuss this question more fully in a future paper.

Yours etc.,
R. F. HUNTER, B.Sc., A.R.C.S., F.C.S., etc.

NOTICES OF BOOKS.

Space and Time, (an Experimental Physicist's Conception of These Ideas and

Their Modification, by CARL BENEDICKS, Formerly Professor of Physics at the University of Stockholm. Translated by J. HARDEN, with an introduction by SIR OLIVER LODGE, F.R.S. Pp. xiv + 98. Methuen & Co., Ltd. London. 1924. 4s. net.

This little volume gives a clear and intelligible account o fthe import of the fundamental conceptions on which our physical sciences are based, together with some historical perspectives illustrating the evolution of this branch of human thought. The author writes in a fluent and captivating style, free from difficulty.

Nascent Oxygen, or The Secrets of Rickets and The White Plague, by HENRY E. JONES, M.B.C.M. Pp. 96. Messrs. Methuen & Co., Ltd., London. 3s. 6d. net.

The author probes at the cause of Tuberculosis, Rickets, and Rheumatism, and explains in plain readable English the composition of Nascent Oxygen and emphasizes its importance as Nature's most powerful germicide, and the inestimable benefits to be derived by the intelligent use of pure water, pure air and open spaces in the prevention and treatment of these maladies.

BREWING INDEX.

The *Collective Index* 1911-1923, of the *Journal of the Institute of Brewing* has just been issued (London: Harrison & Sons, St. Martin's Lane, price 21/-). This index is divided into four parts (1) Authors; (2) Subjects; (3) General Matter; (4) Lists of Journals from which communications have been abstracted.

In the Author index the names are arranged alphabetically but the titles of their communications are in chronological order. The index has been compiled by Mr. W. H. Bird, the Institute's Secretary, with the help of Mr. C. E. Randell.

BOOKS RECEIVED.

A Systematic Course of Qualitative Chemical Analysis of Organic and Inorganic Substances, by HENRY W. SCHIMPF, Ph.G., M.D. Revised by ALFRED J. CONE, Phar.D., Ph.G. Pp. IX. + 201. Fourth edition. Chapman & Hall, Ltd., London. 1924. 1 dollar 75 cents.

The Book of Receipts, Containing a Veterinary Materia Medica, by E. W. LUCAS, G.B.E., and H. B. STEVENS, O.B.E. Pp. 473. Twelfth edition. Messrs. J. & A. Churchill, Great Marlborough Street, London, W.

Analytical Chemistry, by WILLIAM T. HALL. Pp. xiii. + 811—Vol. 11. Sixth Edition. Messrs. Chapman & Hall, 11, Henrietta Street, Covent Garden, W.C.2. 1924. 25s. net.

The Extra Pharmacopoeia, Vol. 1, 18th Edition. Revised by W. H. MARTINDALE, Ph.D., F.C.S., and W. W. WESTCOTT, M.B., D.P.H. Pp. xxxviii. + 1163. Feap. 8vo. 27s. 6d. net.

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Latest Patent Applications.

22557—Badische Anilin & Soda. Fabrik.—Manufacture of organic compounds. Sept. 24th.

22594—Humphrey, H. A.—Ammonia synthesis. Sept. 24th.

22322—Soc. Anon Le Petrole Synthetique.—Synthetic manufacture of hydrocarbons. Sept. 22nd.

Specifications Published This Week.

202975—Rheinische Kampfer Fabrik Ges.—Production of aromatic sulphonic acids.

221716—Soc. of Chemical Industry in Basle.—Manufacture of the phos-

phorous containing nuclear substance of milk casein.

Abstract Published This Week.

220012—Electrolysis.—American Smelting & Refining Co., 120, Broadway, New York, U.S.A.

Tin, obtaining. In depositing tin from impure tin anodes, there is employed an electrolyte containing an organic sulphonic acid, in quantity sufficient to prevent the formation of basic salts of tin and to produce a smooth, dense, and adherent deposit. A suitable electrolyte contains 4 per cent. tin, 5 per cent. sulphuric acid, 2 per cent. hydrofluosilicic acid and 2 per cent. cresol sulphonic acid. Sulphuric acid must be present in excess of the sulphonic acid to ensure precipitation of lead and to prevent solution of lead by the hydrofluosilicic acid. Lead-lined vats may be used. With anodes made from certain ores, the hydrofluosilicic acid may be omitted, 10-15 per cent. sulphonic acid and 2-4 per cent. sulphuric acid being used; in this case it is desirable to add a small amount of glue or other hardening agent. Compounds produced by sulphonating benzol, phenol, toluol or naphthalene may be employed instead of cresol sulphonic acid. A current density of 8 amps. per sq. ft. of cathode surface may be used. A temperature of 95° F. is preferred, the voltage being 0.2 to 0.25, but temperatures up to 130° F. may be used. At 65° F. a voltage of 0.3 to 0.4 is required. The process may be continued until 75-80 per cent. of the anode is dissolved. A certain amount of tin may be dissolved in the electrolyte as a stannous compound before commencing refining. The formation of stannic compounds is undesirable. The electrolyte may be circulated by pumps and heated by steam coils.

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THE CHEMICAL NEWS,

VOL. CXXIX. No. 3367.

MERTON HOUSE, SALISBURY SQUARE,
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THE COMPOUNDS OF QUADRIVALENT NICKEL WITH DIMETHYLGLOXIME AND A DELICATE TEST FOR NICKEL.

(By F. FEIGL (II. Chem. Univ-Institut, Wien).

It has been known for some time that no union has been obtained, with the exception of the higher nickel oxide, by which the existence of a tri—or quadrivalent nickel is formed—unless very slowly. However, from nickel an element of the 8th group is looked for which resembles cobalt and manganese and would appear in a higher degree of valency; in particular trivalent Co. of which there are a number of complex substances, and would probably enter into a higher degree when first a simultaneous secondary valency makes its appearance. K. A. Hofmann and U. Erhardt show that a salt of trivalent nickel can be satisfactorily formed with Formoxime CH_3: NOH but the complex compound becomes $Na_3Ni\ (CH_2NO)_6$. So far a compflex union of quadrivalent nickel is unobtainable.

Statements are found showing that, according to Brunck, in th nickel-dimethylglyoxime precipitate the presence of nitrates interferes with quantitative separation of nickel. The author shows experimentally that ferricyanide, peroxide and permanganate do so also. A red solution results that includes the nickel. Precipitation is completely prevented by dimethylgloxime when it is taken up in presence of lead peroxide and soda lye. An intense red solution is obtained which, under suitable conditions, includes the whole of the nickel. The nickel is here found in a higher degree of valency, for after mixing with potassium iodide and acidifying a marked iodide deposit is formed. A sample of the solution on benzidene paper gives a bluish-brown colouring to the surface.

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CHEMICAL NEWS, MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

For preparation of compound proceed as follows:—5 grams of $NiCl_2 + H_2O$ are dissolved in warm water, mixed with strong soda lye (30 per cent.) and to the nickel hydroxide precipitated add a hot saturated solution of 2 grams of dimethylglyoxime and 5 grams of PbO_2. In addition to the partial formation of nickel-dimethylgloxime, an intense redness is also observed which on heating turns to black (prolonged boiling is to be avoided. In this way the bulk of nickel goes into the filtrate and can be used for wider investigation.

All attempts to isolate the nickel-complex, by contact with the solution at a higher temperature under normal and diminished pressure; by contact "in vacuo" at the room-temperature; and by salting out, are without success.

Uniting the solution in "in vacuo" therefore does not lead to results because the complex salt readily loses water. It is after evaporation only of the remaining water and other portions (free alkali, alkaline salts and lead) that it becomes solid and isoluble in the usual solvents. It is not crystallisable.

Acidifying with mineral or acetic acids bleaches the red solution and disintegrates the complex nickel salt. Thus is isolated a complex salt by careful neutralisation. The dilute acid is allowed to flow in dropwise, on reaching the neutral point a dark-red substance is precipitated. Filter and wash with cold water and alcohol. The dark powder obtained explodes on heating and is insoluble in the usual solvents and water. With dilute acid it separates into Ni-ion and dimethyl-gloxime and then dissolves readily in NaOH, KOH, Na_2CO_3 and NH_3 to a blood-red colour.

ANALYSIS AND CONSTITUTION.

The analysis corresponds with the formula

$$\begin{matrix} DH \\ DH \end{matrix} \Big> Ni:O$$

Results:

Calculated—Ni 19.27, N 18.38

Found—Ni 19.3, 18.8, N 18.65.

The quadrivalency of nickel is the result of a quantitative test. According to above the isolated substance dissolves in soda lye. Divide the solution into two parts. One contains the nickel; the other, on nearly acidifying in presence of KI settles, under iodide mixture in two definite values which proceed from the transition of the higher-valency nickel.

Nickel determination: 10 cc of solution is evaporated with some nitric acid, the residue heated, absorbed in acid and the nickel precipitated as nickel-dimethyl-gloxime. Weighings: 0.0251 gram Nickel-dimethylgloxime = 0.0050 gram Ni.

Iodide determination: 10 cc of the solution is mixed with excess of KI, acidified with HCl and the iodine liberated is estimated. 7.8 cc of N/50 thiosulphate is reuired. From this calculate the liberated quadrivalent nickel-iodide mixture with 0.0198 gm. iodine. From the nickel and iodide found calculate atomic ratio Ni:I=1:1.8, within limits of experimental error proves existence of quadrivalent nickel. Similarly, from a modified experiment where a quantitative determination of nickel mixture is converted into the higher-valency nickel compound, and, as above, oxidation takes place: 3 cc of nickel sulphate solution (1 cc = 0.0121 gr.Ni) is made with dilute soda lye, ammonia, 25 cc of a 1 per cent. alcoholic dimethylglyoxime solution and about 5 gm. of lead peroxide added. At first heat carefully until the disappearance of the reaction, filter (permanent residue is nickel-free), and to the cooled filtrate add 3 gms. of KI and acidify.

For titration of liberated iodine 11.8 cc of N/10 thiosulphate solution are used. Calculated atomic radio Ni:I=1:1.9. (0.1490 gm. of Iodine).

Here the isolated quadrivalent nickel compound may, as the oxidised nickel-dimethyl-gloxime, be taken up; and probably, owing to dehydration with acid a close hydrated compound is formed.

$$[\mathrm{DH\ Ni\ DH.\,.\,2H_2O}](\mathrm{OH})_2 \rightarrow 3\mathrm{H_2O} + \mathrm{Ni\ (DH)_2O}.$$

Preparation of iodide compound: As previously shown make a solution of the complex salts (5 gm. $NiCl_2$ $6H_2O$ of a concentrated iodine-potassium iodide solution containing 5 gm. KI and 6 gm. of I, heat carefully to boiling. A dark, fine crystalline substance is precipitated, filter off and dry. It is allowed to stand in the cold with concentrated iodine-potassium iodide solution for one hour in order to dissolve out impurity of iodine and PbI_2. The KI is removed by washing with water, filter and dry. A dark-red powder is obtained which is insoluble in all solvents with exception of NaOH and NH_3. It splits up with dilute acid into Ni and Iodine-ion. It explodes on heating. Analysis of iodine substance. Calculating from formula

DH Ni DH. . . $.2H_2O$ (OK) (I)

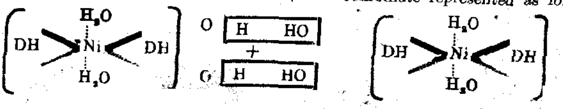
Calculated: N 11.97, Ni 12.54, I 27.13

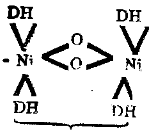
Found: N 12.51, Ni 11.80, 1 26.40

The low Ni and I values with the high N value shows that substance evidently includes some dimethyl-gloxime as well as impurity.

A complex compound exists in the red solution which has amphoteric properties. Because the acid nature increases the solubility in alkali, and the basic nature forms an iodine-bearing compound when the solution is mixed with iodine-potassium iodide.

The dehydration reaction is (analogous with formation of the bichromate from the monochromate represented as follows:—



→ 6 H_2O + 

2 Ni $(DH)_2O$

The use of the formation of quadrivalent nickel for detecting small quantities of
A test which shows that nickel will mix with strong ammonia. Mix together a knife-point of PbO_2, one drop of dilute soda-lye and about 8-10 cc of 1 per cent. alcoholic dimethyl-gloxime solution. Boil briefly and filter. The filtrate is coloured, according to quantity of nickel, a deep-red to reddish-yellow. Whereas a blank test is coloured only faint yellow (probably due to decomposition of the dimethyl-glyoxime by PbO_2).

An idea of the sensitiveness is shown as follows:—The reaction has a saturation limit 2.4 gm. in 4 cc: 2.4 (F_4). Sensitiveness = 1:1666000. The one over against "Tschugaeff's reaction" has a sensitiveness of 1:400000. The test is also of value for colorimetric estimations.

J. C. M.

[Abstracted from the *Berichte*, May, 1924.]

CRITICAL STUDIES ON METHODS OF ANALYSIS.

XIII.: Carbon.

By Leon A. Congdon, Fred J. Brown and R. Kenneth Friedel.

Introduction.

The estimation of carbon has received considerable attention, since the importance of carbon and its compounds is evident and well recognized in every industry, both organic and inorganic. Besides, carbon in organic compounds, has theoretical and scientific importance to the 200,000 or more organic carbon compounds that are known. Thus one finds several hundred investigations cited in the original literature which have for their prime importance the determination of total carbon in some form or other. Particularly is this true in the iron and steel industry where the small per cent. of carbon present has considerable significance in four forms known as iron carbide or cementite, hardening carbon, graphite, and graphitic temper carbon. In general the per cent. elongation and contraction of iron or steel decreases as the per cent. of carbon is increased and the tensile strength and elastic yield point of iron or steel increases as the percentage of carbon is increased.

The greater part of the original references for the estimation of carbon has to do with the socalled dry combustion method where the substance is burned in a combustion tube or similar apparatus in the presence of purified oxygen, the gas being passed over a reduced copper spiral, CuO, or a silver spiral or salts of potassium chromate in order to eliminate nitric fumes if present by reducing them to nitrous fumes, and then purified from other intering gases and water by various reagents in absorption tubes containing silver sulphate, sulphuric acid, phosphorous pentoxide, or calcium chloride. The resulting CO_2 gas gives the weight of CO_2 in the sample examined.

A number of investigations have been made with the so-called wet combustion method for carbon, where the substance to be examined is oxidized by potassium dichromate and snlphuric acid and the resulting CO_2 gas, after being purified in a similar manner as in the dry combustion process, is aspirated into the potash bulb or similar apparatus and weighed.

Numerous references in the literature give methods for the estimation of carhon in the form of CO_2 from carbonates, from gases and air, etc. These are based on the gasometric methods where the CO_2 gas is measured hy volume under standard conditions of temperature and pressure. In the case of carbonates, the CO_2 is generally liberated by HCl, and the CO_2 measured gasometrically.

Colorimetric estimation of carbon, especially in iron or steel, is based on the brown color produced by HNO_3 (1-3) and the intensitry of the color compared with standards of known strength.

Titration methods for carbon have been based on first the combustion of the carbon and then the absorption of the CO_2 in a standard potassium hydroxide or barium hydroxide solution and titration with standard acid for the excess of the alkali not saturated hy the CO_2. Then we have the estimation of bicarbonate in the presence of

carobnate by neutralization methods with use of different indicators or effect of heating.

Some experimental work is reported in the literature for a direct method of carbon, where the mixture is fused with K_2CO_3 in a silica crucible, washed with HCl, then with NH_4OH and the carbon weighed directly.

In addition to the above investigations, Pregl and also Dubsky and other investigators report methods for the estimation of carbon by microanalysis, where small samples are used and weighed out by means of a microbalance. The smallness of the sample, a few milligrams, reduces the time for microcombustion and surety of completeness of combustion.

The investigation reported herein will deal with the three common methods for *the estimation of carbon in a sample* steel, namely, the Wet Combustion methc the Dry Combustion method, and t Colorimetric method.

Experimental.

The sample selected for comparison accuracy was a U. S. Bureau of Standar Basic open Hearth Standard Sample N 13 b. containing a recommended value an average percentage of 0.61 carbon fro eight co-operating analysts by the dire combustion method. The sample also co tanied 0.2% Si, 0.6% Mn, 0.038% S 0.026% P., 0.014% Cu, 0.01% Ni, 0.015 Cr., but no Mo nor V was detected.

The following table shows the results the experimental study of these well-know methods on the sample mentioned above:

TABLE I.

Method Used.	Weight Sample. *Gram.*	Per cent. *Total Carbon* in Sample	Per cent. Total Carbon Obtained.	Aver. per cent. Total Carbon Obtained.	Difference from claimed per cent. Total Carbon.
Direct	1.0239	0.61	0.56	0.51	-0.10
Wet	1.0052		0.49		
Combustion	0.5073		0.47		
Process.	0.4165		0.46		
(Without	0.2740		0.64		
isolation of	0.2639		0.51		
carbon).	0.2000		0.54		
	0.2000		0.49		
	0.2000		0.47		
	0.2000		0.46		
Wet Combustion Process. (First isolation of carbon).	0.2668	0.61	0.59	0.59	-0.02
Dry	0.1000	0.61	0.69	0.59	-0.02
Combustion	0.2000		0.66		
Process.	0.2000		0.57		
(Shimer Pt.	0.2000		0.55		
crucible).	0.2000		0.47		
Colorimetric Process.	0.2413	0.61	0.61	0.56	-0.05
	0.2338		0.59		
	0.2186		0.62		
	0.2140		0.56		
	0.2113		0.52		
	0.1990		0.52		

Before discussing these results perhaps it might be well to tabulate some results obtained in this laboratory by the dry combustion of carbon by means of the Shimer platinum crucible, after inolation of the carbon from the sample by the well-known means of potassium copper chloride solution. This method was tried on different standard steel and iron samples having large and small percentages of carbon claimed for them. Table II. shows the results obtained by various workers in this laboratory so that the personal equation might be eliminated as much as possible.

TABLE II.

Kind of Sample.	Per cent. Total Carbon in Sample.	Per cent. Total Carbon Obtained.	Aver. per cent. Total Carbon Obtained.	Difference from claimed per cent. Total Carbon.
U. S. Bur. Stand. Iron 5 b.	2.726	2.77 2.55 2.61 2.63	2.64	-0.086
U. S. Bur. Stand. ‖22 Steel Bessemer.	0.587	0.58 0.60	0.59	+0.003
U. S. Bur. Stand. ‖8 a. Steel Bessemer.	0.084	0.11 0.14	0.13	+0.046

DISCUSSION OF RESULTS AND METHODS.

It has been noted by Isham (Mattill) and Aumer (1), that the direct combustion of steel for carbon shows results 0.004% higher than results by the solution and combustion method. Levy (2) has noted that in the estimation of carbon in steel by the direct combustion method these high results are due to dissolved CO_2 and CO in the steel which appears as carbon in the direct combustion method and is lost in the solution method. He found that the error may amount to as much as 0.03% carbon or judged by a few samples reported as much as 0.08% to 0.20%. Auchy (3), Gilbraith (4), Hatfield (5), Kohout (6), Parker (7), and Tucker (8) state that the colorimetric process for carbon does not seem to be reliable and gives results lower than the direct combustion method, and some of these investigators state that the colorimetric process for carbon does not seem to be reliable and gives results lower than the direct combustion method, and some of these investigators state that the colorimetric process should be abandoned. Binder (9) states that the condition of the carbon separated out by $Cu(NH_4)_2Cl_2$ solution is dependent upon the C - Fe compounds present.

In this study, the Wet Combustion Method showed considerable difficulty. The combustion train was set up as follows: —Aspirating bottles using water to force air through the train; air purifier filled with soda-lime and phosphorous pentoxide, separating by glass wood; dropping funnel and combustion flask under which was the Bunsen burner; U tube, empty; U tube containing anhydrous silver sulphate and concentrated H_2SO_4 and glass beads; U tube containing calcium chloride; and a Gomberg KOH bulb with side arm with calcium chloride and phosphorous pentoxide. All joints were sealed with paraffin where any rubber connections were necessary and the apparatus was tested for leaks before determinations were made. The sample of steel drillings was placed in the combustion flask with 5 grams of C.P. K_2Cr_2O7, then two to three liters of moisture—CO_2 free air was then passed through the train, after which 100 cc. of concentrated H_2SO_4 was then dropped from the dropping funnel on to the mixture in the combustion flask. Heat was applied to the combustion flask cautiously at first and

then strongly enough to cause a good evolution of CO_2. The difficulty of this method is to ascertain when the evolution of CO_2 has ceased. The best results were obtained under these conditions when the length of time for oxidation was ¾ of an hour. Some trouble was encountered with bumping in the oxidation flask, but this only occurred when the length of time of the run was shortened too much which necessitated use of a hotter flame. A small three-way tube was inserted in the train to try and ascertain when evolution of CO_2 had ceased by passing some gas into concentrated lime water, but this was not very successful. As will be seen from Table I., the average amount of carbon obtained by this method was about 0.10% lower than the amount claimed for the sample by the Bureau of Standards.

The Wet Combustion Method by the same apparatus by first isolating the carbon from the steel by means of potassium copper chloride solution gave results on the average about 0.02% lower than that claimed for the sample by the Bureau of Standards, and although a much longer time is required to first isolate the total carbon, it is a much more accurate process.

The Dry Combustion Process by means of a Shimer (10) crucible, was performed with the following apparatus and train:—Oxygen in tank under pressure with needle valve for regulating flow of oxygen; two glass towers, each containing calcium chloride and soda lime to purify the oxgyen gas; a platinum shimer crucible with copper water jacket to cool the gas, and also an asbestos board to protect from flame except a hole into which the crucible was set; next a combustion tube containing CuO heated by a Bunsen flame in order to further oxidise any carbon monoxide not taken care of by the Shimer crucible; U tube containing glavss wool; U tube containing calcium chloride; a Gomberg KOH bulb for absorption of the CO_2 with a calcium chloride safety tube. The drillings of the steel sample were placed on a layer of previously heated asbestos in the Shimer platinum crucible and no flux was used in these experiments as reported in Table II.. the carbon was first removed from the steel by means of a solution of potassium copper chloride and the combustion of the carbon was determined in a similar manner. The results obtained by this method gave results only 0.02% on the average less than those claimed for the sample by the Bureau of Standards as given in Table I., where the same steel sample was placed in the Shimer crucible. Where this method used on the isolated carbon from a sample of iron or steel as given in Table II., the best results were obtained when about 0.5 gram of the original sample was taken for analysis. Too large samples or too small weights of the sample should be avoided substantiating Bender's experiments where he claims that the carbon separated out by such a solution is dependent upon the C - Fe compound present. The sample giving the best result by this method was one containing 0.6% carbon.

In all these methods, the KOH weighing bulb was counterpoised in weighing by a similar bulb to prevent errors.

The Colorimetric Process for carbon experimented on in this study gave results on the average about 0.05% lower than that claimed for the sample by the Bureau of Standards. This method is much more accurate than the Wet Combustion Process for carbon, where the iron or steel drillings are used directly. It is a very quick method and is used by the industries to a considerable extent. It is probably accurate enough for the manufacturer of steel where quick results are necessary. When using this method, results should be compared with a standard sample, the composition of which is similar to the one analyzed, otherwise incorrect results or conclusions will follow. This was done in this investigation.

Summary and Conclusion.

1. A survey is given of the methods generally used for the estimation of total carbon.

2. Experimental results are given on the analysis of a sample of standard steel put out by the U.S. Bureau of Standards for the percentage of total carbon. The methods examined were the Direct Wet Combustion Process; the Wet Combustion Process by first isolation of the carbon; the Dry Combustion Process by direct method with a Shimer platinum crucible; the Dry Combustion Process by first isolation of the carbon and burning in a Shimer platinum crucible; and the Colorimetric Process for carbon.

3. The authors classify the accuracy of these methods as follows:—1st, the Dry Combustion Process by means of isolation of the carbon and burning in a Shimer

platinum crucible; 2nd, Dry Combustion Process where the sample is directly burned in a Shimer platinum crucible; 3rd, the Colorimetric Process for the estimation of total carbon; 4th, the Wet Combustion Process by first isolation of the carbon; and 5th, the Wet Combustion Process by directly determining the carbon without first isolating it.

References.

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(3) Auchy, Geo.; *Jour. Amer. Chem. Soc.*, 1903, XXV., 999-1000.

(4) Gilbraith; *Jour. Iron & Steel Inst.*, CLXXXI., 234.

(5) Matfield; *Jour. Iron & Steel Inst.*, II., 187.

(6) Kehout, J. F.; *Jour. Ind. Eng. Chem.*, 1911, IV., 378; Wood, E. E.; *Jour. Ind. Eng. Chem.* 1911, IV., 547-8.

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(9) Binder, O.; *Chem. Zeit.* 1913, XXXVI., 1155.

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SODIUM TUNGSTATE.

By Edgar F. Smith.

(Contribution from the John Harrison Laboratory of Chemistry—University of Pennsylvania.)

(Continued from Page 241).

From the data submitted above one cannot escape the conclusion once more that of all the soluble sodium tungstates two are of the first importance—the 1:1 (basic) and the 1:4 (acidic). From these the intermediate members are derived. And stress must be placed on the fact that when an acid of any sort is added to a solution of the 1:1-salt, the 1:4-salt is formed and the latter immediately combines with varying amounts of the normal salt to give rise to one or the other of the intermediates, depending upon the environment of the reaction.

It is well established that the 1:4-salt reverts to the 1:1-salt upon the addition of an excess of alkali, so there came the thought that possibly, with a standardized alkali, the 1:4-salt could be made to retrogress toward the 1:3-salt. This was tested but the 1:3-salt did not appear. The product was, indeed, the 4:10-salt, present very probably in conseuence of the hydrolysis of an unseen, intermediate 1:3-body. Success was also had in changing the 4:10 salt to the 5:12-salt, but the latter did not obligingly pass into the 1:2-salt—no, the normal salt was the only and final product.

In the light of the behaviours described in the preceding paragraphs one need no longe stand in awe of the mystery surroundin the soluble sodium tungstates, although th deportment of the individual members ma need further investigation.

The acidity of sodium meta-tungstate which enables it to unite with the very alka line normal sodium tungstate, enables i further to combine with the normal sodiur molybdate, normal sodium chromate, etc. but these results require further stud before making any statements.

Another curious behaviour was this: o adding tri-sodium phosphate, in aqueou solution, to an equivalent of normal sodiur tungstate, their joint solution stood fc weeks in the cold, eventually yielding goo corps of the two salts which had not com bined to a phospho-tungstate. Howeve upon redissolving the salts and renderin their solution acid by the addition of hydr chloric acid, after the lapse of ten or twel hours, yellow coloured crystals of sodiu phospho-tungstate appeared. Does th mean that in producing the complex deriv tives of phosphorus and tungsten the latt must be in the form of a meta-salt? I other words, when applying para-tungsta of sodium to make phospho-tungstates, to prepare vanado-tungstates, which tun stic acid (that in the normal salt), or that the meta-salt is essential in order to get tl complex acid? Is not the acid in the no mal salt $x\,Na_2O\,.\,WO_3 + y\,Na_2O\,.\,4\,WO$ really changed by the acid in the solution meta-acid, and in the end, is it not th tungstic acid which is involved in the fo mation of the phospho-, vanado-, arsen etc., tungstates? These inquiries, it hoped, will be answered shortly.

In discussing the 5:12-salt, and i potassium and ammonium analogu Scheibler remarked that he had not pr

pared corresponding alkaline earth salts, or metallic salts, because these were not only insoluble in water, but were non-homogenous mixtures and there was, therefore, no object in analyzing them. This statement it was which von Knorre (*Berichte 18, 326*) questioned, and accordingly proceeded to prepare the barium, strontium and calcium salts by precipitating *boiling* solutions of the 5:12-salt, with boiling solutions of barium chloride. He obtained insoluble bodies, which, after being air-dried, were analyzed, and to his amazement he found the ratios of basic oxides to acid oxides to be as 1:2.33, favouring, therefore, the formula $3\ Na_2O\ .\ 7\ WO_3 + Aq.$ for sodium para-tungstate. This disconcerted him to such a degree that he suggested the existence of *two* modifications of the para-tungstates, with the formulas:

$$3\ R_2O\ .\ 7\ WO_3 \text{ and } 5\ R_2O\ .\ 12\ WO_3;$$

and, he further promptly inspired Gonzalez (*Jr. prakt. Ch., 36* (neue Folge) 44 (1887)) to study the other tungstates, *e g.*, copper para-tungstate; but Gonzalez was not able to determine whether it had the formula

$$3\ CuO\ .\ 7\ WO_3\ . + 19\ H_2O,$$
$$3\ CuO\ .\ 7\ WO_3\ . + 19\ H_2O,$$

He made the same comment on the manganese salt; *yet was sure that the silver and* zinc salts were:

$$5\ Ag_2O\ .\ 12\ WO_3 + 8\ H_2O$$
and
$$5\ ZnO\ .\ 12\ WO_3 + 37\ H_2O$$

although he assigned the cobalt and cadmium salts to the

$$3\ R_2O\ .\ 7\ RO_3 + Aq \text{ type.}$$

All the double salts prepared from $5\ Na_2O\ .\ 12\ WO_3 + 28\ H_2O$, gave analytical data *confirming the 5:12 ratio*

$$CuO\ .\ 4\ Na_2O\ .\ 12\ WO_3 + 32\ H_2O$$
$$PbO\ .\ 4\ Na_2O\ .\ 12\ WO_3 + 28\ H_2O$$

$$2\ CoO\ .\ 3\ Na_2O\ .\ 12\ WO_3 + 30\ H_2O$$
$$2\ CaO\ .\ 3\ Na_2O\ .\ 12\ WO_3 + 34\ H_2O$$
$$NaO\ .\ 4\ Na_2O\ .\ 12\ WO_3 + 29\ H_2O$$

Every bit of uncertainty, created by von Knorre's suggestion that there are two forms of para-tungstates, is at once eliminated if it be rememberd that if to cold, not *boiling*, solutions of sodium 5:12-salt, there be added an excess of a *cold* solution of barium chloride, for then the precipitate formed, after washing and drying, invariably analyzed for the ratio 5:12:

Cal. for $5:12 + 24\ H_2O$		Found for $5:12 + 24\ H_2O$	
BaO	19.22%	19.43%	19.42%
WO_3	69.93%	69.83%	69.77%
H_2O	10.85%	10.79%	10.79%

In some instances the total water content was 24 molecules, then 25 molecules, and even 26 molecules, due no doubt to the time during which the salt was permitted to lie in the air. But the ratio between the basic oxide (BaO) and acid oxide (WO_3) remained constant at 5:12. At other times on diluting the 5:12-salt solution the ratio of basix oxide to acid oxide became 3:7, *and on boiling the 5:12-salt solution, prior* to the precipitation with a hot solution of barium chloride, the ratios of basic oxide to acid oxide varied from 5:12, to 5:8, to *7:13, depending evidently upon the degree* of hydrolysis which had taken place in the boiling 5:12-salt solution. Such results warranted Scheibler's surmise that the *precipitates by the alkaline earth salts* and also by metallic salts are non-homogenous mixtures, dependent upon the degree of hydrolysis which prevailed at the moment. Products such as the chromium, bismuth and ferric bodies are doubtful. In them the ratio of basic to acid oxide varies widely —so widely—that Lotz (*Ann. der Chemie, 91, 49*) in his earliest studies of the tungstates refrained from deducing any formulas from the analyses gathered from the aluminium and similar salts. He thought they were heterogeneous mixtures.

(To be continued.)

GENERAL NOTES.

FACTORY AND WORKSHOP.

NOTIFICATION OF DISEASES.

In pursuance of sub-section 4 of Section 73 of the Factory and Workshop Act, 1901,

the provisions of the said section apply to all classes of

(i) Poisoning by carbon bisulphide,
(ii) Poisoning by anilin and its compounds, and
(iii) Chronic benzene poisoning

occurring in a factory or workshop.

This Order, which may be cited as the Factory and Workshop (Notification of Diseases) Order, 1924, shall come into force on the 1st day of January, 1925.

DIAMOND JUBILEE CELEBRATION OF THE L.M. & S. RAILWAY CHEMICAL LABORATORY, CREWE.

The sixtieth anniversary of the establishment of the L.M. & S. Railway Chemical Laboratory at Crewe (the first Railway Chemical Laboratory in the country) was celebrated by the staff (past and present) at a Dinner held at Crewe on October 10th. Captain Beames, M.I.C.E., the principal guest, and Dr. Lewis-Dale, who was in the chair, spoke of the initiative of the old L. & N.W. Railway in recognising as early as 1864 the importance of the application of chemical science to industry.

BRIGHT FUTURE ANTICIPATED FOR BRITISH COLUMBIA NON-FERROUS ORES.

The High Commissioner for Canada in London has received from the Dominion Department of Mines the following article prepared by Mr. A. J. C. Nettell of the Geological Survey Branch:—

Mining operators in British Columbia have been severely handicapped in the past by the lack of a convenient market for their ores. This has been due, partly, to the complex character of the ores themselves, but mainly to the difficulties encountered in the transportation. It is believed, however, that a solution of this principal problem has now been found, and plans are well advanced for the development of an inter-Empire project which aims at the establishment of regular shipments of non-ferrous ores and concentrates from British Columbia to the smelters of the United Kingdom.

FOOD ADULTERATION.

Sale of Food and Drugs Acts.—According to a Blue Book just issued, the total number of samples of food reported upon by public analysts during 1923 was 114,846, it is stated, and of these 6,980, or 6.1 per cent., were reported as adulterated, or not up to standard. For the years 1922 and 1921 the percentages of adulteration were 6.2 and 6.7 respectively, and the percentage of 6.1 for 1923 is the lowest since the Sale of Food and Drugs Act, 1875, came into operation.

The percentage of adulteration in London was 4.6; in the forty largest provincial towns having a population over 100,000, 5.9; in the county districts, 6.7; and in the towns having a population of 100,000 and under, 7.7.

In regard to margarine, the Blue Book says:—"In London two samples of margarine were found to contain small amounts of mineral oil—namely, solidified paraffin, a very undesirable addition which has no food value. The presence of this substance in margarine had not previously been reported for several years."

One sample of "Demerara sugar" consisted of artificially dyed sugar. Four other samples of sugar contained small amounts of grit, ground rice, and sodium bicarbonate, "presumably through accidental contamination."

Not always is advice on national problems supplied by those most fitted to give it. This reflection gives a new importance to a report "On the Encouragement of Fundamental Research" just issued by the National Union of Scientific Workers (25, Victoria Street, London, S.W.1. Price 6d.).

The report deals not only with the value of research to the community, but with the value of creating the research spirit in the community. Science will not be encouraged properly and its full benefits obtained until we all have to a certain extent the scientific outlook.

For the rest, the report deals with the conditions under which research workers should be employed, what inducement is necessary to obtain their services, and how research in general may be encouraged. It is interesting to find a whole-hearted condemnation of patents, prizes, and special grants for successful work. Some at least

of the scientists want the nation to find the best men, to give them security and proper salaries, and to use the results of the work for the common benefit.

The report asks for more money in aid of publication, and suggests that something might be done to co-ordinate the work of the seventy scientific societies which are now responsible for it.

The Report should be read by all those who take an intelligent interest in the problems of modern civilisation.

SMOKE ABATEMENT.

A Conference is to be held in connection with a Smoke Abatement Exhibition in Manchester on November 4th to 6th. It is expected that a very large number will be present at the Conference including delegates from the Municipalities and various Institutions.

The Exhibition includes large Gas and Electrical displays, and there is a full representation of the leading firms interested in matters connected with the Abatement of both Industrial and Domestic Smoke. The production of smokeless fuel by Low Temperature Carbonisation of Coal will form a prominent feature. The use of Towns and Producer Gas in Industry, Mechanical Stokers, Domestic Appliances, Powdered Fuel Firing, Oil Firing, and other methods will receive full attention. An important feature will be the "Ideal Boiler House" which is being designed to illustrate how Fuel Economy and Smoke Abatement can be achieved by attention to the method of firing and the setting of a boiler. The effects of smoke on Health, Building Materials, etc., and the tremendous tax that it makes on the pockets of all will receive full attention.

IMPORTANT ORDER FOR VICKERS

The Foundation Company, Limited, acting on behalf of Messrs. Lafarge, have placed an order with Vickers Limited, Barrow-in-Furness, for the first Clinker Grinding Plant, comprising Tube Mills, installed in this country in connection with the manufacture of Ciment Fondu.

PROCEEDINGS AND NOTICES OF SOCIETIES.

PHYSICS IN INDUSTRY.

The seventh public lecture of a series on this subject being given under the auspices of the Institute of Physics, will be on "Electrical Precipitation" and will be delivered by Sir Oliver Lodge on Wednesday, October 29th, at 5.30 p.m., at the Institution of Electrical Engineers, Victoria Embankment, London. The chair will be taken by Sir Charles Parsons, President of the Institute.

PHYSICAL SOCIETY OF LONDON.

The next meeting of the Society will be held at 5 p.m. on Friday, October 24th, at the Imperial College of Science, South Kensington, S.W.1.

The following papers will be read:—

1. *Underblown Pipes*, by D. GUNNAIYA, M.A., and G. SUBRAHMANIAM, M.A., with Demonstration by D. J. BLAIKLEY.
2. *On the Temperature Gradient in Gases at Various Pressures*, by W. MANDELL, B.Sc., and J. WEST, B.Sc.
3. *Vectorial Dimensions*, by J. F. S. ROSS, M.C., B.Sc.

THE BRITISH ASSOCIATION.

[TORONTO MEETING.

Presidential Address to Section M.—Agriculture, by SIR E. JOHN RUSSELL, F.R.S., entitled *Present-day Problems in Crop Production.*

(*Continued from Page* 244).

But there are more fundamental problems awaiting solution. It is by no means certain that we know even yet all the plant nutrients. The list compiled by Sachs many years ago includes all needed in relatively large amounts, but Gabriel Bertrand has shown that it is not complete and that it is not complete and that certain substances—he studied especially manganese—are essential, although only in very small amounts. Miss Katherine Warington, working with Dr. Brenchley at Rothamsted, has shown that leguminous plants fail to develop in the so-called complete culture solution unless a trace of boric acid is added. Mazé has indicated other elements needed in small amounts.

Another problem needing elucidation is the relationship between the quantity of

nutrients supplied and the amount of dry matter produced. Is dry matter production simply proportional to nutrient supply, as Liebig argued, with the tailing off beyond a certain point, as demonstrated by Lawes and Gilbert, or is it always less than this, as indicated by Mitscherlich's logarithmic curve, or is the relationship expressed by one of the more complex sigmoid curves as there is some reason to suppose? We do not know; and the problem is by no means simple, yet it governs the "diminishing returns" about which farmers now hear so much. Again, very little is known of the relationship between nutrition and period of growth. One and the same quantity of a nitrogenous fertiliser, for example, may have very different effects on the plant according as it is given early or late in life; not only is there a differenc in quantity of growth, but also in the character of the growth, but also in the character of the growth. Late dressings cause the characteristic dark-green colour to appear late in the season, and thus affect the liability to fungoid diseases; they increase the percentage of nitrogen in the grain and they may give larger increases of crop than early dressings.

Investigations are neded to find the best methods of increasing the supply of organic matter in the soil and its value for the different crops in the rotation.

All these problems will sooner or later find some solution. But there remains a greater problem of more importance than any of them: the linking-up of plant nutrition studies with those of the soil solution. As our cousins in the United States were the first to emphasise, the fundamental agent in the nutrition of the plant is the soil solution, and they have made a remarkable series of investigations into what appeared at one time a hopeless proposition—the physico-chemical interactions between the soil and the soil water. Whitney and Cameron began the work, and it has gone on with much controversy—as important scientific investigations always do—and it is now being attacked with much vigour by some of the younger scientific workers, particularly in the Californian school: Burd, Hoagland, Kelley, Lipman, Stewart, Sharp, and others. There is also some valuable work by Gola and other Italians. The natural soil solution is not always the best for the growth of plants. It is reasonable to suppose that the most efficient method of using fertilisers would be for making up the soil solution to the optimum composition and concentration for each stage of the growth of the crop. Unfortunately, this cannot yet be done. The added fertiliser does not simply increase the concentration of the soil solution to the precise extent that might be expected; there are interactions, absorptions, and base exchanges of the kind studied first by Way, much later by van Bemmelen and by Gedroiz, and more recently by Hissink and by Wiegner. Further, the plant relationships are not constant; there is apparently—though this is not certain — more response to certain nutrients at one time of its life than at another. A great advance in crop production may be expected when the soil chemists have discovered the laws governing the soil solution, when the plant physiologists can give definite expression to the plant's response to nutrients, and when someone is able to put these results together and show how to alter the soil solution so that it may produce the maximum effect on the plant at the particular time. The new soil chemistry will yet have its triumphs.

The Soil Micro-organisms: Can they be Controlled?

It is now more than forty years since the discovery of the great importance of micro-organisms in determining soil fertility. Practical applications necessarily lag far behind; but already three have been made each of which opens out great possibilities for the futnre. The long-standing problem of inoculation and leguminous crops with their appropriate organisms has already been solved in one or two of its simple cases, chiefly lucerne on new land, and the new process has helped in the remarkable extension of the lucerne crop in the United States and in Denmark. We believe at Rothamsted that the more difficult English problem is now solved also. Interesting possibilities are opened up by the observation that a preliminary crop of Bokhara clover seems to facilitate the growth of the lucerne.

The organisms effecting decomposition are now coming under control, and are being made to convert straw into farmyard manure (or a material very much like it) without the use of a single farm animal. The process was worked out at Rothamsted, and is being developd by the Adco Syndicate, who are now operating it on a large

scale and are already successfully converting some thousands of tons of straw annually into good manure.

The third direction in which control of the soil organisms is being attempted is by partial sterilisation. This process is much used in the glasshouse industry in England, and it has led to considerable increases in crop yields. The older method was to use heat as the partial sterilisig agent, and this still remains the most effective, but owing to its costliness efforts have been made to replace it by chemicals. Considerable success has been attained; we have found a number of substances which seem promising. Some of these are by-products of coal industries; others, such as chlor- and nitro-derivatives of benzene or cresol, are producible as crude intermediates in the dye industry.

(To be Continued).

INSTITUTE OF MINING ENGINEERS.

PRESIDENTAL ADDRESS.

THE VALUES FOR WHICH THE INSTITUTION STANDS.

(Continued from Page 246).

In saying this, I believe I am saying what all our political parties would subscribe to, however little they speak of it. In any case, I feel confident that I am only describing in words what has been the practice of many eminent mining engineers with whom I have come into close contact, and what corresponds to the underlying sentiment of the Institution as expressed at its ordinary meetings, and still more clearly, perhaps, at its dinners.

There will doubtless always be contentions about wages and other conditions of employment; but these can be, and indeed have been to a very great extent in the past, carried through in a friendly spirit. The special instability which has shown itself recently in the relations between employers and employed depends, as it seems to me, on the idea that has got abroad that the employed are only units in an economic machine manipulated by so-called capitalists without any real sympathy with or understanding of those employed. All real respect for the supposed economic machine is thus lost. It seems like a thing fit to be kicked or hit with a sledge hammer whenever occasion arises.

Now I think we have to dig pretty deep to get at the origin of this idea. At first one is apt to blame the mere size of modern industrial undertakings. In a large colliery, for instance, it is imposible to maintain direct contact between the head management and the men employed. With efficient organization and selection of staff, however, a quite effective indirect contact can be maintained, though I should like to emphasize the necessity of having only men with real human sympathy on the executive staff. I cannot see that mere size has anything really essential to do with the matter.

The more we think, the more we are driven back to the fundamental question whether it is or is not true that an industrial undertaking like a colliery is only an economic machine of which the employed are unit parts. If it is only a machine, then it has no soul to hurt, though it has a body to kick; and the capital represented by it stands for no spiritual value to be respected, even though it be part of the nation's capital. But we are constantly being told about economic machinery, and about laws of economics which, like the laws of mechanics, have no regard for sentiment, and from which there is no escape. Men very commonly accept in practice the metaphor of the machine, taking this metaphor for a complete representation of industrial reality; and it seems to me that wholly unnatural instability in the relations between employers and employed is the result. I am convinced that the real driving force behind what is called labour unrest is just human rebellion against what are regarded as inhuman relations.

Had the prevailing sentiment and practice of the members of this Institution not been altogether inconsistent with acceptance of the metaphor of the machine, you would, I know, never have invited me to be your President. In the strength of this knowledge, I will try to examine the metaphor. It is evidently a part of what is commonly believed to be modern realism. We must all bow before reality: mere sentiment is in the long run only a will-o'-the-wisp. If, as so-called modern realism teaches, our world consists of self-existent material things and separate individuals each actuated by self-interest, then these things and individuals behave in accordance with definite laws which we can discover by comparatively simple investigation. We are free to believe, if we like, that God made

the material things, the individuals, and the laws of their behaviour; but this does not matter at all so far as ordinary practical affairs are concerned.

If we enquire whence the so-called realism came, we find that it very gradually took form in science, philosophy, literature, and theology: only at a latter time coming to be applied in connexion with the relations between employed and employers. In the grey light of this realism spiritual values seemed to melt away from the visible world, as the phantastic appearances of night melt away at dawn; but only to leave a drab world of physical and economic reality.

There is no use in denouncing physical science and economics as mere materialism. If we want things done, and if we want to avert troubles and dangers from those we care for, we must act in the light of physical and economic knowledge. The more of this light we can throw on practical affairs, and the further that light enables us to see into the fnture, the more effectively can we help onr fellow-men. Those responsible for the guidance of coal-mining undertakings have constantly to be saying no, in the light of economic and engineering knowledge, to well-meaning but short-sighted proposals, as well as seeking for what will really promote these undertakings; and those who cannot say no quite clearly are not suited for the positions they occupy.

It is one thing, however, to make use of physical and economic knowledge, but quite another to regard this knowledge as by itself an adequate basis for practice. Here this Institution would, I feel confident, refuse to acknowledge the drab world of physical and economic realism. The capital of a mining enterprise is its credit; but that credit depends upon the faithful and loyal service of all those engaged in the enterprise, from the lowest paid to the highest paid. Conversely, it depends on careful and loyal care for the interests in the widest sense of all those engaged. The relation among those connected with the enterprise is one of comradeship, and if this relationship is not realized and acted on the enterprise is unstable and its credit or capital may disappear. A working coal-mine is no mere outcome of what are called economic and physical conditions: it is the outcome of human comradeship, which uses in its own way, and at its own free will, the tools provided by physical and economic knowledge. It has thus a spiritual value capable of inspiring the highest and most unselfish form of service: its credit in the economic sense is credit in a deeper spiritual sense.

These are mere dogmatic statements. What is the justification for them? Does not actual experience force us back to the drab world of economics in which spiritual values do not count, to the world of each man or group of men pulling against his neighbours? What I wish to maintain as representing this Institution is that actual experience as we meet it in British collieries is not the drab experience of abstract economics, and that the psychology which represents each individual as simply striving after his own individual interests is bad psychology so far as it is applied to British pitmen, whatever position they may occupy in the industry.

(To be continued.)

NOTICES OF BOOKS.

Teoria de las Valencias Positivas Y Negativas, por el P. Ignacio Puig, S.J. (Professor of Mineral Chemistry at the Institute Químico de Sarriá, Barcelona) Tipografia Catolica Casals, Calle Caspe, 108 (apartado 776), Barcelona, 1924.

In this pamphlet of 31 pages the author deals with atomic structure and chemical compounds. As an example, the nitrogen atom contains 5 outer electrons and 3 gaps all arranged on an outer circle, the electrons representing 5 positive valencies and the 3 gaps 3 negative valencies. The next circle, of less diameter, has 2 electrons diametrially opposite to each other. Another inner concentric circle of slightly less diameter has also 2 oppositely placed electrons, these being one quarter way round from the others. The central neucleus has an encircling ellipse carrying 1 proton, this evidently in revolution. Within this ellipse are four groups, 3 contain 3 protons and 1 electron each, while the fourth groups contains 4 protons and 2 electrons. In a periodic table after P. Saz, hydrogen has an atomic number 1, an element above helium an atomic number 2, a missing element below hydrogen at atomic number 3, while helium is given the atomic number 4. Uranium has therefore its atomic number raised to 94. In a periodic classification, the elements are grouped so as to agree

with numbers 4×1^2, 4×2^2, 4×3^2. Hydrogen is shown having one outer electron (+ valency) and one gap (- valency) these electric valencies appearing on one circle (diametrically opposite to each other) with a central nucleus. About 12 pages are taken up with chemical equations based upon + and - valencies etc. In the bibliography only the following names appear:—Abegg, Cabrera, Graetz, Lewis, Lowry, Noyes, Puig, Saz, Fry.

The Structure of Matter, by J. A. CRANSTON, D.Sc., A.I.C. Pp. xv. + 196. London: Blackie & Son, Ltd., 50, Old Bailey, E.C.4. 1924. 12s. 6d. net.

During the past last few decades there has been an advance of unexampled rapidity in experimental knowledge bearing directly on the question of the constitution of matter. Few chemists have the time to follow the developments of this new atomic science by a study of the original literature, and depend upon the volumes that are published from time to time, giving an account of the advances made. There are now a number of books dealing with the atomic theories that the student has a wide choice.

The present volume is suitable for advanced examination candidates for those chemists who are not specialists in this field. It includes an account of the periodic law, the nature of valency, and the structure of chemical compounds, which are considered in relation to the electron as the fundamental unit in chemical action. Langmuir's Octet Theory of valency is discussed in considerable detail.

The methods which have been used to determine the charge and mass of the electron are given with good illustrations. Radioactivity, the experiments of Moseley, atomic numbers, and the nuclear theory of the atom, isotopes and the researches of Aston, the work of the Braggs on crystal structure, and Bohr's theory of spectra, are the subjects of other chapters.

Charts of the Chemical Reactions of the Common Elements, by JOHN A. TIMM, Ph.D. Pp. 81. New York: John Wiley & Sons, Inc. London: Chapman & Hall, Ltd., 11, Henrietta Street, Covent Garden, W.C. 1924. 10s. net.

These charts of the reactions (with lists of equations) of the 30 commoner elements have been compiled to aid students in their revision work.

the student's best course would be to make summaries himself.

The Eastman Kodak Co. has just published the seventh volume of *Abridged Scientific Publications*.

The volume includes the scientific papers emanating from the Kodak Research Laboratory, which have appeared in various journals during 1923.

These communications are of a very high order of merit and include important investigations on the chemical and physical problems of photography.

Among the papers included are the following: "A Laboratory Fractionating Column," by H. T. Clark and E. J. Rahrs. "An Adaptation of the Thallofide Cell to the Measurement of Photographic Densities," by A. L. Schoen. "Quantum Theory of Photographic Exposure," by L. Silberstein. "Chemistry of the Acid Fixing-Bath," by S. E. Sheppard, F. A. Elliott, and S. S. Sweet.

Exposure theories and other matters of immediate photographic interest are also discussed in other papers.

Messrs. Longmans Green's Catalogue, Paternoster Row, London.

This well-known firm of publishers issues a handsome catalogue of 196 pp., with an elaborate index in alphabetical order of pp. xliv.

Licht and Farbe in Kolloiden, by VON Prof. Ostwald's *Licht und Farbe in* . xiv. + 556. Leipzig and Dresden: Vertag von Theodor Skeinkopff. 1924. $7.50 unbound; $8.30 bound.

That books have their fate, like human beings, is true of this work. It is stated in the preface that the revised proofs were stamped June and July, 1914. The War cut short not only the author's work but also that of the printer and publisher. The claims upon the author's time have further delayed the publication of this monumental work, since ample leisure is essential for the revision of so important a book.

Prof. Estwald's *Licht und Farbe in Kolloiden* is stated to he the first part of an extensive treatise on Disperse Systems. To read every line of the 500 odd pages is in itself a task; to understand it all thoroughly is the privilege of comparatively few. The first chapter deals with optical heterogeneity and is followed by one discussing the

fraction, diffraction and other causes of this phenomenon are described in detail. This leads up to an account of the ultra-microscope and its uses. The latest instruments available are described, as well as those of Siedentopf and Zsigmondy.

Other chapters are concerned with Polarisation; Adsorption; Refraction, and Surface Colours and Double Refraction. Very little of the matter has appeared previously in textbooks, most of the work having been compiled from the original papers scattered through the literature.

The illustrations, many of them of a very high order, call for special mention. The coloured ones of the ultra-microscopic particles show a perfection in photography as well as in the branches of science to which they apply.

The October number of the *Edinburgh Review* includes an article on the history of the well-known publishing firm of Longman's, founded in 1724. It is an interesting story not only because it describes the development of a large firm, but also because it throws light on the changing social conditions. In earlier generations the number of people who read was very small in comparison with the vast numbers of potential readers called into being by the Education Acts passed since 1870. Though few could read, in earlier generations, there was a considerable demand for solid tomes. Life was more leisurely in the eighteenth century than now.

Another interesting point made by the writer is that the publication of expensive books was formerly undertaken by several firms jointly.

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications:

23211—Saderberg, I. W.—Manufacture of nitric acid. Oct. 1st.

23112—Riedel Akt-Ges. J. D.—Manufacture of barbituric acid derivatives. Sept. 30th.

23227—Schwalbe, C. G.—Treatment of sulphite cellulose waste liquor. Oct. 1st.

23136—Stephen, H. — Manufacture of aldehydes and intermediate products. Oct. 1st.

Specifications Published This Week.

221956—Casale, Dr. L.—Apparatus for the catalytic production of synthetic ammonia.

Abstract Published This Week.

220413—Sulphur dioxide, sulphuric acid; selenium, treating gases electrically.—Krafft, M., Parkstrasse, Hruschau, Czecho-Slovakia.

Burner gases are purified for the production of pure sulphuric acid by separating dust, then passing through a washing apparatus such as a tower in which they come in contact with water or dilute sulphuric acid at such a rate that the vaporization and condensation occurring in the washer is not such as to remove the suspended matter from the gases but only such as to increase the size of the suspended particles so that they can be readily separated in a separate apparatus, preferably an electric precipitator. The suspended matter, particularly selenium, is thus obtained in a concentrated form in the precipitator instead of as a sludge in the washer. The sulphur trioxide produced catalytically from the purified gases, is separated as sulphuric acid in a similar manner by passing the gases first through the washer and then through the electric precipitator.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

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CHEMICAL NEWS, MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

THE STRUCTURE OF ANTIMONY.

By HAWKSWORTH COLLINS, B.A. (CAMB.).

In *The Chemical News*, 1920, CXXI., 183, the constitution of Sb was given as AgC =

$$Ag—H—Li—H—H_3$$

This formula explains its atomic weight, the reason for its being diacidic ($H-H_3$) and tribastic (Ag-H-Li), and shows why it is always found with Ag.

In the following calculations 119 has been employed as its atomic weight in accordance with the investigation published in *The Chemical News*, 1920, CXXI, 157.

The above structure will now be proved to be correct quite independently by means of the laws of relative volume and heat of formation.

TABLE I.

The Relative Volumes of Antimony.

Sb	=	Ag	+	C
21.29	=	13.29	+	8.0
18.25	=	10.25	+	8.0
14.00	=	13.29	+	0.71

TABLE II.

Experimental Data Illustrating Table I.

	Relative Volume.	Theor. S.G. at 15° C.	Obs. S.G.
(281)	Sb_2O_3 2(21.29) + 2(2.51 + 4.45 = 52.05		5.251 Playfair
		5.5	5.566 Mohs
(282)	Sb_2S_3 2(21.29) + 2(10.51) + 15.53 = 79.13	4.22	4.223 23° Cooke
(283)	$2Sb_2S_3 + Sb_2O_3$ 2(79.13) + 52.05	4.54	4.5 - 4.6 Dana
(284)	Sb_2S_3 2(21.29) + 3(10.51) = 74.11	4.51	4.516 Hauy
(285)	$PbS.Sb_2S_3$ 20.45 + 15.53 + 74.11	5.2	5.21 18° Hillebrand
(286)	$PbS.Sb_2S_3$ 17.42 + 15.53 + 74.11	5.34	5.30 - 5.35 Dana
(287)	Sb_2O_5 2(21.19 + 7.53 + 2.51) + 4.45	4.74	3.779 Playfair & J
			6.525 Boullay
(288)	$SbCl_5$ 21.29 + 15.085 + 4(23.01)	2.31	2.316 Chem: Kal.
(289)	$SbAs_3$ 21.29 + 3(11.38)	6.206	6.203 Rammelsberg
(290)	$CuSbS_2$ 9.54 + 21.29 + 2(10.51)	4.745	4.748 Rose
(291)	$NaSbO_2 + 3H_2O$ 11.85 + 21.29 + 2(2.51) + 3(14.03)	2.841	2.864 Terrell
(292)	SbI_3 (monoclinic) 21.29 + 3(27.75)	4.78	4.768 22° Cooke
(293)	SbI_3 (hexagonal) 18.25 + 3(27.75)	.	5.01 10° Bodeker
		4.93	4.848 24° Cooke
(294)	Sb_2O_5 2(18.25) + 5(2.51)	6.5	6.525 Boullay
(295)	$Pb(SbO_2)Cl$ 17.42 + 18.25 + 2(2.51) + 15.085	7.04	4.02 Flajolot
(296)	$Sb_2(OH)_2O_3$ 2(18.25 + 2.51 + 5.76) + 3(2.51)	5.28	5.28 Blum
(297)	$Cu_2Sb_4S_7$ 2(9.54) + 4(18.25 + 7(10.51)	5.02	5.03 Cumenge
(298)	Sn_2Sb 2(16.02) + 18.25	7.06	7.07 19° Bodeker
(299)	$(SbO)_2SO_4$ 2(18.25 + 4.45) + 29.45	4.89	4.89 Chem. Kal.

(300)	K_2SO_4 2(18.05) + 29.45	2.654	2.653 14° Wise
(301)	$CuSO_4$ + $5H_2O$ 9.54 + 29.45 + 5(14.03)	2.282	2.284 Thorpe
(302)	$BaSO_4$ 24.58 + 29.45	4.294	4.294 Schweitzer
(303)	$BaCO_3$ 24.58 + 20.55	4.343	4.35 Kirwan 4.30 Karsten
(304)	$SrSO_4$ 19.56 + 29.45	3.75	3.738 18° Schweitz
(305)	$SrCO_3$ 19.56 + 20.55	3.69	3.68 - 3.714 Dana
(306)	$SbBr_3$ (liq.) 21.29 + 2(23.09) + 27	3.80	3.64 90° Kopp i.e., 3.8 15°
(307)	$SbBr_3$ (solid) 21.29 + 2(23.09) + 18.06	4.16	4.148 23° Cooke i.e., 4.16 15°
(308)	CsBr 29.89 + 18.06	4.438	4.433 25° Nostrand
(309)	CsI 29.89 + 27.75	4.510	4.510 25° Nostrand
(310)	TlBr 19.2 + 18.06	7.63	7.54 22°, 7.56 17° i.e., 7.58 15° Keck
(311)	TlCl 19.2 + 15.085	7.0	7.00 Willm
(312)	Ag_3Sb_2 3(9.78) + 2(14.0)	9.75	9.6 - 9.77 Petersen
(313)	Ag_6Sb_2 3(9.78) + 3(10.25) + 2(14.0)	10.0	10.027 Petersen
(314)	NiSSb 7.13 + 10.51 + 14.0	6.64	6.5 20° Rammelsberg 6.803 Jannasch
(315)	Ni_2S 2.(7.13) + 10.51	6.055	6.05 Playfair & J
(316)	ZnSb 14.82 + 14.0	6.384	6.384 Cooke
(317)	Zn_2SiO_4 + H_2O 2(14.82) + 28.08 + 14.03	3.35	3.36 Wieser
(318)	Li_4SiO_4 4(5.46) + 28.08	2.40	2.39 Nostrand
(319)	$SbCl_3$ 21.29 + 2(15.085) + 23.01	3.03	3.064 26° Cooke
(320)	Sb 17.91	6.65	6.646 Playfair 6.675 Spring

TABLE III.

Heat of Formation of Sb		Original Volume.		Rel. Vol. in combination at 15° C.		Change of Volume
-48200	= 120 × (-3.38) × 119	17.91	=	11.29	-	3.38
aq. -50400						

TABLE IV.
Experimental Data Illustrating Table III.

		Theor.	Obs.	Corresponds in Table II. with No.
Sb_2O_3 -2(48200) + 2(96155) + 71515	=	166343	166900	281
Sb_2O_5 -2(48200) + 2(32341 + 96155) + 71515	=	232107	231200	287
liq. $SbCl_5$ -50400 + 63870 + 4(23010)	=	105510	104870	288
Sb_2S_3 -2(48200) + 2(49459) + 30681	=	34199	34400	282
$SbCl_3$ -48200 + 2(56786) + 23010	=	88382	91390	319
aq. $SbCl_3$ -50400 + 2(63870) + 23010	=	100350	100300	
$SbBr_3$ -48200 + 2(45244) + 17000	=	59288	61400	306

The atomic weight of chlorine has been taken as 35.5 in this and preceding papers, because it is generally agreed that the two isotopes, 35 and 37, always occur together in such a proportion as to cause the atomic weight of the element to appear as 35.5. *Cl is the only element whose atomic weight* has not been taken as a whole number in *these papers.*

The atomic weight of bromine has been

taken as 80, because the two isotopes 79 and 81 appear to be always present in about equal proportions. Another volume for bromine, 18.06, is introduced for the first time in Table II. and will frequently appear later. Also a third volume 29.45 for the radical SO_4 is here brought in for the first time and will frequently appear later; so that the three volumes of SO_4 are as follow:—

$$35.61 = 15.53 + 2(7.53) + 2(2.51)$$
$$29.45 = 15.53 + 2(4.45) + 2(2.51)$$
$$30.59 = 15.53 + 7.53 + 3(2.51)$$

SUMMARY.

Antimony is shown to be similarly constituted to the other pentads bismuth and arsenic (*The Chemical News*, 1924, CXXIX, 2 and 205)

As = Cu + C
Sb = Ag + C
Bi = Au + C

and the proof that the structure is correct consists in the facts

(1) that each one of the three volumes can be split up into volumes which have previously been demonstrated for Ag and C;

(2) that one of the volumes, the commonest, is supported exactly by the law of heat of formation, and gives the correct original volume of the element.

The strength of the position will probably be more evident from the following summary:

(1) Ag(107) + C(12) = Sb(119).

(2) A monad + a tetrad = a pentad.

(3) Sb is a non-metal owing to its free H - H_3

(4) 21.29 is shown to be a volume of Sb at 15° C in 14 molecules.

(5) 18.25 is shown to be a volume of Sb in 7 molecules.

(6) 14.0 is shown to be a volume of Sb in 4 molecules.

(7) 13.29 was shown to be a volume of Ag (*The Chemical News*, 1924, CXXIX., 222) in 8 molecules.

(8) 10.25 was shown to be a volume of Ag (*loc. cit*) in 19 molecules.

(9) 8 was shown to be the volume of an atom of carbon, when two of its valences are united to the two of an atom of oxygen, in hundreds of molecules sent to the Nobel Institute in 1914.

(10) 0.71 was shown to be the volume of an atom of carbon, when each valence is united to a separate atom or group, in hundreds of molecules sent to the Nobel Institute in 1914.

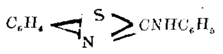
(11) The heat of formation falls in exactly with the law, giving an original volume which in its turn gives the correct specific gravity of the element.

(12) No one of the volumes 21.29, 18.25, 14.0, 13.29, 10.25, 8.0, 0.71 can be altered in the slightest without upsetting a very large number of facts. (This is a statement which applies to all the relative volumes of elements so far demonstrated in *The Chemical News*).

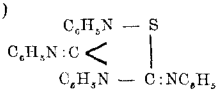
THE SYNTHESIS OF TRIHETERO-ATOMIC FIVE MEMBERED SULPHUR NITROGEN RING SYSTEMS. PART I. THE BROMINATION OF THIO UREAS IN ALCOHOLIC SOLUTIONS AND THE PREPARATION OF BROM 3:5 DI IMINO 2:4 DIPHENYL TETRAHYDRO 1:2:4 THIODIAZOLE AND 3:5 DIPHENYL-IMINO 2:4 DIPHENYL TETRAHYDRO 1:2:4 THIODIAZOLE.

By R. F. HUNTER, B.Sc., A.R.C.S., F.C.S.

The influence of the solvent employed in the bromination of aromatic thio ureas of the type of phenylthiourea and diphenyl thiourea has been already noted by a number of investigators; and the action of halogens on thio ureas under different conditions has been the subject of a number of researches, amongst which may be cited the investigations of Otto (*Berichte*, 1869, II., 409), of Hofmann (*Berichte* 1869, II., 453), of Belstein and Kurbatow (*Berichte* 1874, VII., 730, 1489, 1650), of Claus (*Berichte* 1874, VII., 235), of Mac Gowan (*Jour. f. prakt Chem.* 1886, (2), 33, 188, and *Chem. Soc. Trans* 1887, LI., 378), and of Hugershoff (*Berichte* 1901, XXXIV., 3130). Hugershoff observed (*Berichte* 1903, XXXVI., 3121) that when diphenylthiourea is brominated in chloroform solution, there is formed the red crystalline bromo addition product of 1 phenylaminobenzothiazole (I) whilst when the bromination is carried out in absolute alcoholic solution, a trihetero five membered sulphur nitrogen ring is formed, which is shown to be 3:5 diphenylimino 2:4 diphenyl tetrahydro 1:2:4 thiodiazole (II)

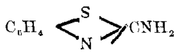


(I.)



(II.)

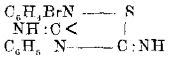
In a similar manner Hugershoff had previously observed that the products of bromination of phenylthiourea in alcoholic and chloroform solutions were different. When phenylthiourea is brominated in chloroform solution, red crystals of what Hugershoff regarded as the tetrabromide of carbamin ophenyliminodisulphide are deposited, from which the so called free carbaminophenyliminodisulphide can be obtained by the reducing action of sulphurous acid followed by treatment with alkali. (*Berichte* 1901, XXXIV., 3130). Actually Hugershoff found at a later date that the so called carbaminophenyliminodisulphide so prepared is identical with the aminobenzothiazole obtained by the action of ammonia on 1 chlorobenzothiazole (*Berichte* 1879, XII., 1129 and 1880, XIII., 11) and which is known to be 1 amino benzothiazole (III.).



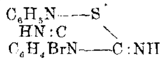
(III.)

While when phenylthiourea is brominated in absolute alcoholic solution there is obtained the bromo derivative of 3:5 di imino 2:4 diphenyl tetrahydro 1:2:4 thiodiazole, which has the constitution (IV) or (V). The 3:5 diphenylimino 2:4 diphenyl tetrahydro 1:2:4 thiodiazole obtained by the action of bromine on an alcoholic solution of diphenylthiourea was further shown to be the same as that obtained by Hector by the action of hydrogen peroxide on diphenylthiourea (*Berichte* 1890, XXIII, 357) and further it was found that the brom 3:5 di imino 2:4 diphenyl tetrahydro 1:2:4 thiodiadole obtained in the bromination of an alcoholic solution of phenylthiourea is identical with the bromo compound obtained by Hector by the action of hydrogen peroxide on phenylthiourea.

In view of the fact that the bromination of various thio ureas and related compounds in solutions of different solvents are at present being examined in this laboratory with the object of extending the synthesis of 1 amino benzothiazole to more complex cases, it appeared of interest to examine the action of bromine on alcoholic solutions of phenyl thiourea and diphenylthiourea under the conditions given by Hugershoff. It was found that an excellent yield of the bromo 3:5 di imino 2.4 diphenyl tetrahydro 1:2:4 thiodiazole (IV) or (V).



(IV)



(V)

is obtained in the form of the hydrobromic acid salt. But the troubles brought about by resinification described by Hugershoff in the case of 3:5 diphenylimino 2:4 diphenyl tetrahydro 1:2:4 thiodiazole, were experienced and the yield of diphenyliminodiphenyltetrahydrothio diazole even in an impure state was poor. It might be noted that bromo diiminodiphenyltetrahydrothiodiazole was nitrated to give a yellow nitro derivative by fuming nitric acid, this derivative has not as yet been investigated.

EXPERIMENTAL.

The phenylthiourea was obtained by condensing phenylisothiocynanate obtained by the hydrochloric acid hydrolysis of diphenylthiourea with alcoholic ammonia.

Diphenylthiourea.

This was worked up from aniline, by condensing the latter with carbon disulphide and alcohol containing a little potash by the usual method of refluxing the materials on a boiling water bath for four hours, using a double surface condenser, the top of which is in communication with a soda lime tower to absorb the sulphuretted hydrogen produced during the condensation. 100 gms of aniline were used to a run. The crude condensation product washed with dilute acid, water and spirit and air dried and used for the preparation of phenyl mustard oil.

Phenyl isothiocyanate.

100 grams of diphenylthiourea were mixed with 350 ccs of strong hydrochloric acid in a litre flask connected to a condenser and receiver. The mixture was slowly heated to boiling over a sand bath and then distilled over a wire gauze. The acid distillate poured into a separating funnel containing three times its volume of cold water and the phenyl mustard oil withdrawn into a distilling flask containing fused calcium chloride. The mustard oil was allowed to stand over the latter overnight and then distilled, using an air condenser, the first fraction being rejected. A second distillation is unnecessary.

Phenylthiourea.

10 gms. of phenylisothiocyanate, 10 gms of ethyl alcohol and 30 ccs of 880 ammonia were mixed in a 500 cc flask fitted with a condenser and the mixture refluxed at its boiling point for ten minutes on a sand bath. The liquid was poured hot into a beaker and allowed to cool, when the phenylthiourea separated in fine white crystals in theoretical yield melting as recorded.

Brom 3:5 di imino 2:4 diphenyl tetrahydro 1:2:4 thiodiazole.

5 grms of phenylthiourea obtained above were dissolved in 100 gms of warm absolute ethyl alcohol in a 350 ccs beaker, and the beaker cooled to room temperature. A burette was then charged with liquid bromine. 7 ccs of bromine were slowly added from the burette to the solution with constant stirring, a milky precipitate of sulphur was first produced, which redissolved to give a clear red solution towards the latter end of the halogen addition. The liquid was stirred, allowed to stand for ten minutes, and nearly the whole of the solvent removed on a steam bath. White crystals form during the removal of the solvent and on cooling, the bottom of the beaker becomes solid with white crystals of the thiodiazole. The crystals were filtered and recrystallised from the minimum quantity of hot water. In this way 4.6 gms of fine white crystals of the hydrobromic acid salt of the bromo derivative of diminodiphenyltetrahydrothio diazole melting 242° to 244° were obtained.

The free base can be obtained by treating the white crystals with 2N caustic soda, bromo diminodiphenyltetrahydrothiodiazole is practically insoluble in cold water, but readily dissolves in a mixture of alcohol and benzene.

Nitro derivative.

A small quantity of the HBr salt of bromo di imino diphenyltetrahydrothiodiazole was dissolved in fuming nitric acid, the nitric acid solution allowed to stand for half-an-hour, and then poured into water, when an orange precipitate of presumably a nitro derivative was obtained. Neither the preparation of the nitro derivative nor the nitro derivative have so far been examined, owing to the progress of other work.

3:5 Diphenylimino 2:4 diphenyl tetrahydro 1:2:4 thiodiazole.

The diphenylthiourea used in this preparation was obtained in fine silvery plates by recrystallising the 100% thiocarbanilide of the B.D.C. with spirit.

5 gms of diphenylthiourea were dissolved in 100 ccs of absolute ethyl alcohol and bromine gradually added to the solution until a permanent orange solution was obtained, 2 ccs of bromine were necessary for this. A vigorous reaction took place when the halogen was first added to the alcoholic solution and a yellow precipitate of sulphur was produced in the liquid which did not redissolve. The mixture was allowed to stand for a few minutes after the completion of the addition and then transferred to a tightly corked conical flask and steadily shaken, when the sulphur coagulated with the production of a clear yellow liquid. The yellow solution was then poured into 400 ccs of cold water, when a white suspension was obtained; strong ammonia was then added with stirring until the liquid was fairly strongly alkaline. A yellow brown resinous precipitate was obtained, which was allowed to remain in contact with the alkaline liquid for six hours and then filtered. The product was still resinous and was allowed to dry in the air for several days. During this time it became hard and was then crushed up in a mortar, and washed with a little water and dried.

The Chemical Laboratory,
Highbury New Park, N.5.

THE INSTITUTION OF ELECTRICAL ENGINEERS.

WIRELESS SECTION MEETING.

On Wednesday, 5th November, 1924, at 6 p.m. (Light refreshments at 5.30 p.m.).

An Address will be given by Mr. E. H. Shaughnessy, O.B.E., Chairman of the Section.

GENERAL NOTES.

HARVEIAN ORATION.

Sir Archibald Edward Garrod delivered the Harveian Oration on October 18th at the Royal College of Physicians, Pall Mall East, London.

They might, he said, associate the names of William Harvey, the physician to King Charles I., and the immortal founder of modern physiology, and Thomas Sydenham, the soldier of the Parliament, who did for clinical medicine what Harvey did for physiology, and brought it back from the realm of fancy to the bedside study of signs and symptoms. The first attempt to start clinical teaching within a university was made in Padua in the late 16th century, but the first organised clinic was that in Leyden, started about the year 1630. Now that the foundation had been well and truly laid, the clinical medium of to-day was able to advance on scientific lines, and the study of the abnormal could be based upon a knowledge of the normal. It was natural, nay, inevitable, that as medical science grew and advanced some of the workers should elect to follow the path which led through the laboratory, whereas to others the wards made a stronger appeal. From the ranks of the clinical workers had been drawn those who, in the past, had built up medical science. It was in the intervals of their clinical practice that such men as Harvey himself, William Gilbert, Nehemiah Grew, and Thomas Young carried out the researches which rendered them for ever famous, and, indeed, clinical medicine was in its essence scientific. But it was an art as well as a science, and in the sick room many qualities were called for which were not essential in the laboratory. Bouillaud described clinical and pathological physiology as the sister of experimental physiology, and since the middle of the 19th century an immense amount of knowledge of the functions of the brain and spinal cord had been acquired by the labours of a band of brilliant investigators, of whom many were their own countrymen.

Obviously clinical medicine presented immense fields of scientific research, and those who cultivated these had the added satisfaction of knowing that every advance of medical science would bring in its train some forward movement in the healing art.

DOMINION BUREAU OF STATISTICS, CANADA.

The Dominion Bureau of Statistics, Canada, has issued the *Annual Report of the Mineral Production of Canada During 1922.*

In comparison with preceding years the mineral production in 1922 was very creditable and was only exceeded in value by the records established in 1918 of $211,301,000 and in 1920 when the peak of $227,859,000 was reached.

The principal mineral-producing province was Ontario, the value of its mineral production being determined as $65,866,029. British Columbia came second with a mineral production valued at $39,423,962; Alberta was third with $27,872,136; Nova Scotia ranked fourth with $25,923,499. The other provinces followed in the order named: New Brunswick, $2,263,692; Manitoba, $2,258,942; Yukon Territory, $1,785,573; and Saskatchewan, $1,255,470.

Seventeen products contributed 98.59 per cent. of the total recorded value of the mineral production of Canada in 1922 and in order of the values assigned these were: coal, gold, cement, silver, clay products, nickel, stone, natural gas, lead, copper, asbestos, sand and gravel, zinc, lime, gypsum, cobalt and salt.

The outstanding feature of the metal production was the excellent gain made in the output of gold by Ontario and British Columbia. The total gold production showed an increase of 36.3 per cent. on that of 1921.

Increased prices and better markets for silver and lead were reflected in excellent gains. Silver advanced 37.1 per cent. in quantity and 48.2 per cent. in value, while lead production rose 39.9 per cent. and the value increased 51.9 per cent. over the record for the previous year.

Nickel and copper were lower than in 1921, although the advance in the price of copper checked the decline in value to 3.78 per cent. as compared with a 10 per cent. decrease in quantity. Nickel fell off 8.8 per cent. in both quantity and value. The smelter production of blister and converted copper in British Columbia was less than in 1921, but the recovery and rise in price of copper did not occur until about the middle of the year and some important copper mines which were active in 1921 did not appear on the shipping list until nearly the close of the year, when there was a de-

cided improvement in the copper industry. The inactivity of the smelting departments of the International Nickel Company in the earlier part of the year and of the British America Nickel Corporation throughout the entire year accounted for the small production of nickel.

The increase in the output of zinc was further emphasized by the rise in price of this metal to an average of 5.716 cents per pound for the year, as compared with 4.655 cents in 1921, both quotations from the St. Louis market. The 6 per cent. increase in quantity resulted in a 30.1 per cent. advance in the total value reported.

The year-end saw a marked revival in the production of cobalt which raised the year's production to 569,960 pounds valued at $1,852,370. Compared with 1921 data, these figures showed 126.1 per cent. greater quantity and 145.0 per cent. increase in value.

Among the non-metallics the output of coal, considering the great loss of time through strikes, was most encouraging.

The output of coal from Canadian mines during twelve months of the calendar year 1922 was 15,157,431 tons, valued at $65,518,497, as compared with 15,057,493 tons, valued at $72,451,656 in 1921; 16,946,764 tons valued at $82,496,538 in 1920; and 13,919,096 tons, valued at $55,622,670, in 1919. The great strike which tied up the United States coal mines or several months was reflected in Canada and resulted in a loss of 1,222,288 working days. Fifteen disputes between employees and employers occurred in the coal-mining industry in Canada during the twelve months ending December, thirteen of which were in Alberta and south-eastern British Columbia, and the other two in Nova Scotia. In all 25,251 men were affected, and o fthe time lost, 931,960 days were lost in the strike which began on April 1st, and 290,328 days' time was lost in the short strikes originating later in the year. Having in mind the fact that over one million working days' time was lost by the employees of the coal mining industry during the year, the output of fifteen million tons may be considered quite satisfactory. Alberta coal mine output amounted to 5,990,911 tons, a little more than half of which was lignite and nearly all the balance bituminous. Nova Scotia contributed 5,569,072 tons and occupied second place among the coal-producing provinces. British Columbia accounted for 2,927,033 tons, and Saskatchewan and New Brunswick followed with 382,437 tons and 287,513 tons respectively.

Sales of cement during the year reached a total of 6,943,972 barrels, or 1,191,087 barrels more than in the previous year, the production being about evenly divided between the plants in the provinces of Ontario and Quebec. Eleven plants were operated during the year.

The manufacture of clay products in Canada, including brick, firebrick, fireclay, fire-proofing, hollow building blocks, sewer-pipe, pottery, terra-cotta and drain tile, was carried on in 232 plants in Canada during 1922, in which the total capital employed amounted to $31,168,903. Production showed a 29 per cent. increase over the preceding year's production to a total of $11,438,456.

Building stone, both rough and dressed, was produced in greater quantity than in 1921, and monumental and ornamental stone also showed improvement in the quantity and value of the output. The kinds of stone quarried in Canada were granite (trap rock, syenite and other igneous rocks), limestone, sandstone, and marble. Total production of all grades was valued at $5,989,864.

The output of natural gas from Canadian fields in 1922 amounted to 14,682,651 thousand cubic feet valued at $5,846,601. The output was greater than in the preceding year and the total value assigned showed a very great increase, due to the fact that the price of the gas to the consumer was used in computing the value in 1922, whereas in previous years the values given were those received by the producer. The difference in these quotations is accounted for by the existence of pipe-line companies who purchase gas from the producers and distribute it to a large number of individual consumers scattered over wide areas.

CHEMICALS AND FOOD.

Last year the following Departmental Committee was appointed to enquire into the important subject of the addition of preservatives to food:—Sir Horace Munro (Chairman), Professor W. E. Dixon, Sir A. D. Hall, Mr. J. M. Hamill, Professor Gowlands Hopkins, Mr. G. R. Leighton,

Mr. A. P. Luff, Mr. C. Porter, Mr. E. Richards, and Mr. G. Stubbs.

The Committee has now completed its labours. In its report, the Committee states that the term preservative is not to include salt, saltpetre, sugar, vinegar, acetic acid, alcohol, spices, or the agents introduced into food by the process of curing known as "smoking." By the term preservative in this report is meant any other substance which, when added to food, has the property of preventing, arresting, delaying, or masking fermentation or putrefaction of food.

Preservatives are stated to be used at present in a somewhat haphazard way, or as a trade custom, or even in ignorance. The committee rejects the plea that they are harmless. It groups them under three headings:—

Group 1.—Formaldehyde and its derivatives and the fluorides.

Group 2 (not so undesirable) includes boric acid and salicylic acid and their salts.

Group 3 (least harmful).—Benzoic acid and sulphurous acid, and their salts.

The conclusion is reache dthat, if preservatives in foods are necessary at all, they should be derived solely from those in Group 3.

This is of great importance because at present the majority of "preserved" foods are doctored with chemicals of the group 2 series. Boron preservatives are largely used in butter, cream, margarine, imported liquid eggs, sausages, potted meat, potted fish, and some beverages; they are also used for packing bacon and hams for export to this country, and are occasionally dusted over these articles of food. Very large amounts are sometimes found. Thus, 175, 140, and 110 grains per pound of boric acid have been found in margarine, butter, and bacon respectively. As a rule, however, the quantity of the substance used does not exceed and rarely amounts to 35 grains per pound. One trade representative told the committee that 52 grains per pound was necessary for his product. Curiously enough, most of the articles in which this preservative is largely used are made and put upon the market by one firm or another without any preservative at all.

Salicylic acid and its salts are found in a number of articles, mostly beverages, including beer, gingerbeer, and cordials, and also in some jam. As many as 17 grains per lb. have been found in sausages. Benzoic acid and sulphurous acid are also in use, but are less obnoxious. The Report svtates:—

"It is evident that at present individuals may consume quite considerable quantities of preservatives in the course of an ordinary day's diet. It is easy to imagine a reasonable meal which might contain 20 or even more grains of boric acid besides other preservatives."

It may be interpolated that eight grains of boric acid is sometimes given as a dose in certain cases of illness. In these cases the doctor always exercises care to see that the patient's digestion is not upset.

The Committee recommend:—

"That the use of preservatives should be prohibited in all articles of food and drink offered or exposed for sale, whether manufactured in this country or imported, except in a few definite and specific cases."

Only two preservatives are to be permitted, benzoic and sulphurous acids and their salts. This is the same conclusion as was reached in America. The principal exceptions in favour of which preservatives are to be allowed are:—Sausages, jam, dried fruit, fruit pulp, beer, cider, wines, cordials, and fruit juices. In all these the suggestion is that sulphur dioxide should be permitted in definite quantities. Benzoic acid may be used as an alternative in certain wines and cordials, in sweetened mineral waters, and in coffee essences. The use of copper salts in the "greening" of peas is entirely condemned. The preservative used must be declared on the label.

Labelling Preservatives.

"The presence of preservatives in food, whether imported or not, should be declared in a manner to be prescribed by the Minister of Health. It is possible that there may be some cases in which the declaration of the preservative used might be difficult to enforce or which might result in undue harm to the industry without compensating advantage to the consumer. If this be so, exceptions might be made in their favour, but in all cases, and in particular that of sausages, we are of opinion that the use of any preservatives in foods should be accompanied by a declaration of the nature and amount of preservative used."

The Committee emphasizes the deficiency in this country of means of transport suitable for foodstuffs as well as the lack of facilities for refrigeration. It recommends

the labelling of all "food preservatives" so that the nature of their contents is exposed. It deals also with colouring matters, and suggests that only certain of these should be permitted.

FOOD AND DRUGS ADULTERATION IN 1923.

While adulteration is still far too prevalent, there was a general improvement in 1923, the percentage of adulteration in 1921, 1922 and 1923 respectively being 6.7, 6.2, and 6.1. In London the percentage was down to 4.6; while in large provincial towns with over 100,000 inhabitants it was 5.9, and in towns under 100,000 inhabitants 6.7, and in rural districts as high as 7.7. Milk was the article subject to most adulteration, London being lowest with 3.8, as compared with Liverpool, 8.7 per cent.

To shew how milk is handled in certain places concrete instances are pointed out:

1.—Defendant was "seen, after taking delivery of his milk from a farm, to add to it water from a dirty cattle trough." The Public Analyst's certificate of a sample of this water showed that it was grossly contaminated and "contained myriads of micro-organisms, green deposits and fungus growths." A fine of £10 and costs was inflicted.

2.—The number of samples reported as containing sediment or dung was 4.2 per cent. of the total number reported as adulterated, as compared with 3.6 per cent. in 1922.

A total of 45 samples were reported agianst for containing a preservative, chiefly boric acid, and in ten of these other forms of adulteration were detected.

GOVERNMENT LABORATORY.

The Report of the Government Chemist for the year ending 31st March, 1924, shews the increasing activity of the Government Laboratory Staff together with the important nature of its activities.

The total number of samples examined in the course of the year, including those dealt with at the chemical stations, is 390,421, as compared with 343,453 in the preceding year, an increase of 46,968. There has been an increase of more than 21,000 in the number of samples examined at the chemical stations, while the number examined at the central laboratories in London has risen from 225,073 to 251,009 an increase of 25,936. The samples of wine have increased from 85,776 to 92,319, of sugar from 49,172 to 55,887, and of tea from 36,518 to 42,068, while there are notable increases in the number of samples of wort, exported beer, and spirituous preparations. The number of samples of beer for the detection of dilution is again high, the number being 5,079. The number of samples of imported beer has risen from 1,361 to 15,283, and of exported tobacco and snuff from 8,533 to 17,718. Both these large increases are due to the establishment of the Irish Free State, and the necessary examination of goods passing to and from that country. The work in connection with the Safeguarding of Industries Act has involved the examination of nearly 8,000 samples. The Dangerous Drugs Act and the Dyestuffs (Import Regulation) Act, continue to impose considerable work on the Department.

Chemical Work.

Chemical work is performed for the Admiralty in connection with the Contract Department at Whitehall, the naval yards, *the engineering department*, the hospitals, and the Medical Branch. The Contracts Branch of the Admiralty submitted 97 samples of food on tender, for report as to conformity with specification and opinion as to relative merits. The technical examining officers at the victualling yards forwarded 230 samples from supplies for examination and report, many of the samples being submitted with the object of preventing the issue of canned goods contaminated with metals. Medical officers sent two samples of milk supplied to hospitals. Other samples to the number of 81 included soaps, fabrics for sail cloths, filter cloths, tin plates, and gilded badges.

The total number of samples for the Admiralty was 410. This number does not include the sea water samples forwarded by the Admiralty for the determination of salinity.

Hydrometers, Saccharometers, Thermometers and Graduated Vessels.

Hydrometers, for ascertaining the strength of spirits; saccharometers, for use at

breweries, distilleries, and glucose factories, thermometers and graduated vessels of various descriptions for use in the Surveying Department, are tested at the laboratory as to their accuracy before being issued to the officers of Customs and Excise. During the past year, 1,817 such tests were made. In addition, 162 instruments were examined for the South African Government, and two Sikes' hydrometers were tested for the National Physical Laboratory by comparison with the Revenue standard instruments deposited in this laboratory.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

Some investigations have been carried out at the request of the Co-Ordinating Board of the above Department. Thus, in connection with that Board's work on formaldehyde, a series of experiments was made on its recovery by means of water. A small experimental tower strung with coir-yarn was used, when it was found that water passing down the fibres, absorbed formaldehyde from air in which it was present in small concentration.

The chemical and physico-chemical investigation of the ammonium sulphate-nitrate involved in the explosion at Oppau was undertaken, and the results, together with those obtained by the Research Department, Woolwich, on its explosive properties, were described at a meeting of the Faraday Society on the 14th April, 1924.

Sea Water. The sea water samples are examined in connection with a scheme of oceanic research carried out by the Fisheries Departments of the Crown acting in concert with the work of the International Council for the Exploration of the Sea. One of the objects of the investigation is to determine the influence upon fish life of the salt concentration or salinity. In order to make the results obtained by the different countries concerned in the work comparable with one another, a prepared standard sea water is issued from a central bureau, and a uniform process is followed in the determination of the salinity. The samples are taken by ships using certain frequented routes, by lightships, and by cruising research vessels; and observations are made at the same time of the temperature, depth, geographical position, &c. The results are also frequently made use of by the Admiralty in connection with their experimental work. The salinity of 5,757 samples, including 1,048 received from the Admiralty, was determined during the year under review. In addition, 131 samples of sea water were examined for the amount of dissolved oxygen present.

Chemical Stations.

In order to avoid delay in the examination of samples, chemical stations have been established at the more important seaports and one inland town, where samples are tested by Customs and Excise officers who have been specially trained at the Government Laboratory for this purpose. The chemical station at Liverpool is in charge of one of the chemists on the staff of this Department. The table in Appendix B shows the samples examined during the year, the numbers being including in those given under the appropriate heads below.

As a check on the work of these officers, the residues from a certain number of samples tested by them are re-tested at the Government Laboratory. The number of such re-tests during the year was 1,015. The results indicate that the work at the chemical stations is performed in a highly efficient manner.

Dangerous Drugs Act.

Under the provisions of the Dangerous Drugs Act, the importation or exportation of prepared opium is prohibited. The Act, further, makes it an offence, *inter alia*, to import or export without licence certain drugs (morphine, diamorphine (heroin), cocaine and ecgonine) or preparations containing more than a certain percentage of these drugs. In suspected cases the officers of Customs and Excise sample the goods and the samples are examined here; 94 such samples were received, and of these 24 were found to contravene the provisions of the Act. Two samples marked "morphiumpulver" were seized by the officers, but they were found to consist of lactose.

Various.

Various substances, such as sulphur, asafoetida, sago flour, tar oil, carbolic and cresylic acids, moss litter, soda ash, borax, asafoetida, sago flour, tar oil, carbolic and cresylic acids, moss litter, soda ash, borax, hellebore, cayenne, lampblack, saltpetre, and anthracene oil are used in denaturing tobacco. One hundred and seventy-eight

samples of nicotine preparations, of which 79 were from imported goods, were examined, and approved for delivery free of duty.

STAFF.

It might be added that the technical staff of the Department consists of:—The Government Chemist, Deputy Government Chemist, 5 Superintending Chemists, 10 Chemists Class I, 25 Chemists Class II., 30 Temporary Assistant Chemists.

In addition, 80 Officers of Customs and Excise are seconded for service in this Department.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE BRITISH ASSOCIATION.

[TORONTO MEETING.]

Presidential Address to Section M.—Agriculture, by SIR E. JOHN RUSSELL, F.R.S., entitled *Present-day Problems in Crop Production.*

(*Continued from Page* 262).

Looking back over the list of problems it will be seen that they are all too complex to be completely solved by any single worker. Problems of crop production need the co-operation of agriculturists, plant physiologists, soil investigators, and statisticians. Even plant breeding necessitates the help of a physiologist who can specify just what the breeder should aim at producing. And this gives the key-note to the period of agricultural science on which we have now entered —it is becoming more and more a period of co-operation between men viewing the problem from different points of view. Good individuals working at the same institution. tinue to be done, but the future wil undoubtedly see a great expansion of team work such as has already led to important results in medical research, and such as we know from our experience at Rothamsted is capable of giving admirable results in agricultural science.

The team work should not be confined to indibiduals working at the same institution. The world gain greatly if co-operation such as now exists between the Imperial College Botany School and Rothamsted could be effected between other great institutions devoted to agricultural science in the various countries of the world. To take only one illustration: how much could be accomplished in the study of the very difficult alkali problem if it were possible to organise a team representing such great agricultural stations as, for instance, California and Utah, the Departments of Agriculture of India and other of the great Dominions affected, Rothamsted, Hissink's school, with power to lay down experiments anywhere and money to carry them out. And if extended co-operation of this kind should prove impossible of attainment, much could be done by fostering co-operation between the Agricultural Institutions of the Empire. There are certain great problems which are common to large parts of the Empire where the experience of one part would be of great value to the rest. The institutions in Britain, for example, have experience of problems connected with land long since settled and brought into cultivation, where men must produce 40 or more bushels per acre of wheat and 6 to 10 tons per acre of potatoes to make these crops pay, and where animal husbandry must be run on sound and economic lines. Canada has an unrivalled experience with wheat, and in the Western provinces has a magnificent chance for studying one of the most important problems of the day—the water supply to the crop. Australia, New Zealand, South Africa, East, West, and Tropical Africa, India, the West Indies—to mention only a few in the great family that forms the British Empire—all have their special lines in agricultural development; each has some achievement that can be shown with pride and in the certainty that its study will benefit others. The Empire has already its Conference of Premiers, why should it not have its conference for agricultural science and practice?

With fuller co-operation both of men and of institutions we could do much to overcome the present difficulty in regard to utilising the information we already possess. In the last thirty years an immense stock of knowledge has been obtained as to soils and crops—knowledge that ought to be of supreme value in interpreting the facts of Nature as shown in the field. It is stored in great numbers of volumes which line the shelves of our libraries, and there much of it rests undisturbed in dignified oblivion. In the main it consists of single threads followed out more or less carefully; only rarely

does some more gifted worker show something of the great pattern which the threads compose. But even the most gifted can see but little of the design; the best hope of seeing more is to induce people to work in groups of two or three, each trained in a different school and therefore looking at the problem from a different point; each seeing something hidden from the rest. Unlike art, science lends itself to this kind of team work; art is purely an individual interpretation of Nature, while science aims at a faithful description of Nature, all humanistic interpretation being eliminated. There is certainly sufficient goodwill among the leaders of agricultural science to justify the hope of co-operation; there are probably in existence foundations which would furnish the financial aid.

And that leads to my last point. What is the purpose of it all? Team work co-operation, the great expenditure of time and money now being incurred in agricultural science and experiment—these are justified only if the end is worthy of the effort. The nineteenth century took the view that agricultural science was justified only in so far as it was useful. That view we now believe to be too narrow. The practical purpose is of course essential; the station must help the farmer in his daily difficulties—which again necessitates co-operation, this time between the practical grower and the scientific worker. But history has shown that institutions and investigators that tie themselves down to purely practical problems do not get very far; all experience proves that the safest way of making advances, even for purely practical purposes, is to leave the investigator unfettered. Our declared aim at Rothamsted is "to discover the principles underlying the great facts of agriculture and to put the knowledge thus gained into a form in which it can be used by teachers, experts, and farmers for the upraising of country life and the improvement of the standard of farming."

This wider purpose gives the investigator full latitude, and it justifies an investigation whether the results will be immediately useful or not—so long as they are trustworthy. For the upraising of country life necessitates a higher standard of education for the countryman; and education based on the wonderful book of Nature which lies open for all to read if they but could. How many farmers know anything about the remarkable structure of the soil they till, of its fascinating history, of the teeming populating of living organisms that dwell in its dark recesses; of the wonderful wheel of life in which the plants take up simple substances and in some mysterious way fashions them into foods for men and animals and packs them with energy drawn out of the sunlight—energy which enables us to move and work, to drive engines, motor-cars, and all the other complex agencies of modern civilisation? No one knows much of these things; but if we knew more, and could tell it as it deserves to be told, we should have a story that would make the wildest romance of human imagination seem dull by comparison and would dispel for ever the illusion that the country is a dull place to live in. Agricultural science must be judged not only by its material achievements, but also by its success in revealing to the countryman something of the wonder and the mystery of the great open spaces in which he dwells.

INSTITUTE OF CHEMISTRY EXAMINATIONS.

The candidates mentioned below have passed the examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland:—

General Chemistry. — Allister, C. F., Heriot-Watt Coll., Edin.; Austin, R. G., Univ. Coll., Southampton; Bell, J. L., Heriot-Watt Coll., Edin.; Brown, J. Heriot-Watt Coll., Edin.; Browne, T. E. W., B.Sc. (Wales), Univ. Coll., Bangor; Cochrane, C. G., B.Sc. (Lond.), Heriot-Watt Coll., Edin.; Firth, H., Bradford Tech. Coll.; Fletcher, A. E., Central Tech. School, Liverpool; Hallas, C. A., B.Sc. (Lond.), Northern Polytechnic Inst., and King's Coll., Lond.; Lander, Miss C. M., Univ. Coll., Nottingham; McGill, A., Heriot-Watt Coll., Edin.; Ransome, G. L., B.Sc. (Lond.), The Univ., Camb.; Rumford, F., Battersea Polytechnic; White, W. A., Sir John Cass Technical Inst.; and Williams, K. A., B.Sc. (Lond.), Chelsea Polytechnic Inst.

Metallurgical Chemistry.—Claudet, R. A. O., B.Sc. (Lond.), King's Coll., Lond., and Sir John Cass Technical Inst.

The following candidates have passed the examinations for the Fellowship:—

Branch A: Inorganic Chemistry.—Morris, E. A., B.Sc. (Lond.).

Branch D: Agricultural Chemistry.—Pyne, G. T., A.R.C.Sc.I., B.Sc. (Lond.).

Branch E: The Chemistry, including Microscopy, of Food and Drugs, and of Water.—Bagnall, H. H., B.Sc. (Birm.).

Branch G: Chemical Engineering.—Sensicle, L. H., B.Sc. (Lond.).

THE CHEMICAL SOCIETY.

PAPERS READ AND DISCUSSED AT THE ORDINARY SCIENTIFIC MEETING, OCT. 16.

The Influence of Catalysts on Carbonisation, by R. LESSING and M. A. LISTER BANKS.

The catalytic effect of individual mineral constituents on the carbonisation of coal, to which attention had been drawn by Lessing in 1914, has been studied. As the ash in coal cannot be reduced below a certain minimum, sugar and cellulose, practically free from ash, were investigated in the first instance. Forty catalysts have been tried, the compounds being added at the rate of 0.01 gram molecule per 100 grams of sugar or cellulose, either in solution or dry. On carbonising the material by the platinum crucible method for the determination of volatile matter in coal (for three minutes only), remarkable difference in coke yields were found, varying from 20 per cent. to 5 per cent. of the sugar or cellulose, the untreated coal being always at or near the bottom of the list. An attempt was made to group the added compounds according to the magnitude of their coke-yielding effect. The quantitative variation is equalled if not surpassed by extraordinary differences in appearance and structure and particularly the swelling propensities in the case of sugar. A preliminary study of coal was made by examining the clarain and vitrain fraction of Dalton Main Coal, the ash of which was reduced to 0.86 per cent. Similar variations were obtained in the yield of coke, retort carbon and tar.

The Photosensitive Formation of Water from its Elements in the Presence of Chlorine, by R. G. W. NORRISH and E. K. RIDEAL.

Weigert showed qualitatively in 1908 that when a mixture of hydrogen, chlorine, and oxygen is illuminated water is formed. This reaction has been investigated quantitatively at atmospheric pressure in the present research. This purely photosensitive process of water formation is regarded as independent of the simultaneous formation of hydrogen chloride which occurs. The anticatalytic effect of oxygen on the latter reaction is attributed to a direct intervention of oxygen in the hydrogen chlorine reaction chains with their resultant shortening and the formation of a relatively negligible quantity of water.

The Directive Influence of Substituents in the Glyoxaline Nucleus on Substitution in the Benzene Nucleus of Phenylglyoxalines the Nitration of 2-phenylglyoxaline and its Carboxylic Acids, by F. L. PYMAN and E. STANLEY.

By the mono-nitration of 2-phenylglyoxaline and its 4-mono- and 4:5-di- carboxylic acids, followed by decarboxylation in the last two cases, the isomeric nitrophenylglyoxalines have been isolated in the following yields:—

	p	*o*	*m*
From 2-phenylglyoxaline	50	1.5	0.2
From 2-phenylglyoxaline-4-carboxylic acid	52	—	18
From 2-phenylglyoxaline-4:5-di-carboxylic acid ..	19	—	52

It was suggested that the results are connected with the fact that the first two compounds form salts with mineral acids, whereas the last does not, and on this basis they may be partly systematised with the help of the theory of induced alternate polarities.

THE OPTICAL SOCIETY.

A meeting of the Optical Society was held at the Imperial College of Science and Technology on Thursday, 9th October, 1924, when the following papers were presented and discussed.

"Some Problems in the Theory of Optical Diffraction," by E. T. HANSON, B.A.

The diffraction of waves by a perfectly reflecting wedge is now a problem of considerable celebrity.

A semi-infinite plane may be looked upon as a wedge whose internal angle is zero. The application of Kirchoff's formula in the latter case is considerably extended, it being shown that, through a region of not too small dimensions comprising the whole of the boundary of the geometrical shadow,

the solution thus obtained is identical with *the accurate solution.* An expression is found for a plane wave incident at any angle upon a semi-infinite screen.

The diffraction of waves by a straight slit in a plane screen is a problem not yet exactly solved; it is one which occupied Lord Rayleigh's mind for many years. An approximate expression is found for the disturbance distributed over the slit due to a wave incident normally, and by an application of Kirchoff's formula an important result is obtained very readily, which is in agreement with Rayleigh's investigation by very long analysis.

This appears to be the first time that an attempt has been made to apply Kirchoff's formula to an area of disturbance which is not considered to be uniform over the area.

The paper gives a brief treatment of the foregoing points of novelty and interest in these two problems which have long been and still are of some importance in mathematical physics.

"The Annealing and Re-annealing of Glass," by W. M. HAMPTON, M.Sc., A.I.C.

The factors which play an important part in the annealing glass are discussed. Relations connecting the strains present when cooling commences, strain due to gradient, and strain present after cooling are obtained and the equations are applied to the case of slabs. Tables showing the proportion of temporary strain remaining as permanent strain for different kinds and sizes of slabs are given. The considerations affecting the temperature at which annealing is carried out and the conditions for the total annealing and cooking times to be a minimum are then dealt with, the results being applied to a particular case. The effect of errors in pyrometry are discussed and tables giving annealing temperatcre, annealing time and rate of cooling for various kinds of glass are included.

INSTITUTE OF MINING ENGINEERS.

PRESIDENTAL ADDRESS.

THE VALUES FOR WHICH THE INSTITUTION STANDS.

(*Continued from Page 263*).

It is just a fact of experience that we care for one another's interests, and anyone who goes underground in a British pit can verify that fact much more quickly than he usually can on the surface. He meets comradeship there; and comradeship in service is what unites us all and transforms the drab world of economics into a variegated world of spiritual values. In the brighter light of better psychology the drab uniformity disappears.

The job of a pitman, and particularly of a mining engineer, is not a soft job; but it is a man's job, and the job of a whole man, not the mere economic man who is scarcely half a man. Those who seek for soft jobs, or think they can make mining into a soft job, had better take themselves off to Utopia; they are not wanted in British pits, nor are hypochondriacs or neurasthenics. When we realize what we are working for, and in comradeship with those we care for, hard work and the facing and conquering of dangers and troubles become an honour and not a mere hardship. We then see that physical and economic realism is not realism at all, but a mere superficial representation of a deeper spiritual reality which is in us and around us all the time. In fighting the difficulties and dangers of mining work; in fighting for the economic stability of mining undertakings; including the interests of shareholders; and in fighting for the highest welfare of those employed and their families, a mining engineer finds that spiritual reality in his comradeship with those around him. But it is only in the fight that he and the other pitmen who work with him can find it. If mining ever became a soft job, I think that all true British pitmen would with one accord take to some other more worthy occupation.

In this connexion there comes into my mind a very earnest and truly eloquent speech, made at the time of the great coal-strike by your then President at a dinner of our sister Institution. He expressed his conviction that the only real remedy for labour troubles lay in a more adequate knowledge of one another and then with it a quickened sense of religion. It was assuredly not mere theology that Colonel Blackett had in mind, but practical religion—conduct based on a conviction of the reality of spiritual values and of their dominating influence in all human affairs. What is it that has been undermining that old conviction? It is the idea that the ultimate reality of Nature is expressed in the conceptions of physical science, and that the reality of industrial undertakings is expressed in the conceptions of economic science. There is thus no room left for spiritual reality in ordinary affairs.

THE ROYAL SOCIETY.

A meeting will be held on 6th November, at 4.30 p.m., at which several interesting papers will be read.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The Eightieth General Meeting will be held at the House of The Royal Society of Arts, John Street, Adelphi, W.C.2., on Tuesday, November 4th. The following paper will be read: "The Oilfields of Argentina," by Campbell M. Hunter, O.B.E., M.A., F.G.S., A.M.Inst.C.E., F.R.G.S.

ROYAL INSTITUTION.

The General Meeting of the Royal Institution, Albemarble Street, Piccadilly, W., will be held on November 3rd, at 5 o'clock.

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

23708—Cederberg, I. W.—Catalytic combustion of ammonia-oxygen mixtures. Oct. 7th.

23835—Knoll & Co.—Preparation of dihydrocedeinone from thebaine. Oct. 8th.

Specifications Published This Week.

211831—Texas Gulf Sulphur Co.—Burning of sulphur.

217247—Chemische Fabrik Vorm Sandoz.—Process for the manufacture of the cardiac glucoside of bulbus scillae.

207196—Farbenfabrikenvorm F. Bayer & Co.—Process for obtaining sulphur from a gas containing hydrogen sulphide.

208721—Campagnie Nationale De Matieres Colorantes Et De Produits Chemiques.—Process for the manufacture of perylene.

222158—Electro Metallurgical Co.—Production of non-oxidizing non-brittle sheets, or articles wholly or partially made of sheets, of chrome iron alloys.

Abstract Published This Week.

220,771—Hydrocyanic acid. — Badische Anilin & Soda Fabrik. Ludwigshafen-on-Rhine, Germany.

Hydrocyanic acid is prepared by the interaction of carbon monoxide and ammonia, or by the dehydration of formamide or ammonium formate, using as catalyst an alumina having a vitreous surface with a transparent and microporous body. The alumina may be obtained by precipating a solution of an aluminium salt such as the nitrate with ammonia, washing and drying the product and heating it rapidly. Other metal oxides or hydroxides, e.g. of thorium, zirconium and uranium, may be precipitated with the aluminium hydroxide or may be added subsequently, provided they do not affect the vitreous and transparent character of the product. Other bodies, e.g. grains of silicates, may also be mixed with the alumina. For the production of hydrocyanic acid, a mixture of carbon monoxide and ammonia, together if desired with other gases such as hydrogen or nitrogen, is passed over the contact mass maintained at a temperature of 500-700° C. Alternatively, formamide or ammonium formate, which may be prepared by the interaction of carbon monoxide and ammonia under pressure in the presence of water, is passed over the contact mass at a temperature of 300° C.

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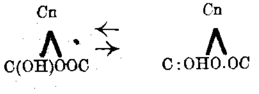
RING CHAIN TAUTOMERISM PART I. THE OCCURRENCE AND EFFECT OF KETO ENOL TAUTOMERISM BETWEEN A RING COMPOUND AND ITS OPEN CHAIN ISOMERIDE AND THE EFFECT OF THE GEM DIETHYL GROUP ON THE TETRAHEDRAL ANGLE.

By R. F. HUNTER, B.Sc., A.R.C.Sc., M.S.Chim., F.C.S.

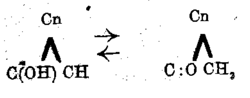
In this series of papers, of which this forms the first part, it is intended to deal with the work of Thorpe and Ingold and their collaborators on the phenomenon which has been termed ring chain tautomerism. Representing ordinary keto enol tautomerism as in A

$$.CHC:O \rightleftarrows C:C.OH \qquad (A)$$

it can be assumed that if the conditions which allow keto enol tautomerism are present in an open chain and a ring compound, that is to say, if the distance apart of the atoms forming the tautomeric complex of the keto enol type A is comparable with that of the atoms forming a potentially tautomeric system between an open chain and a ring compound, the possibility of the occurrence of a new type of tautomerism, which may be termed ring chain tautomerism arises, the two types of which can be represented by B and C



(B)



(C)

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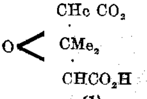
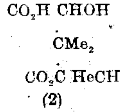
and further there can be no question that under suitable circumstances tautomerism of both types B and C can occur in the same compound. Tautomerism of the type C has been recorded in the antranol anthrone change and also in the transformation of apotricyclol into campenilone (*Ber.* 1921, LIV., 1327). During a search of the literature for other samples of this type of change, the acid prepared by Balbiona by the oxidation of camphoric acid appeared to possess somewhat peculiar properties (*Berichte* 1895, XXVII., 2133) Balbiona showed that the acid on reduction passed into a $\beta\beta$ trimethylglutaric acid. Balbiona considered that the acid contained a hydroxyl group on account of the fact that he was able to prepare both an acetyl and benzoyl derivative from the dimethyl ester, but he did not assign any definite formula to the acid. His work was at a later date repeated by Mahla and Tiemann (*Berichte* 1896, XXVIII., 2151) in the hope of obtaining evidence of the latter's formula for camphoric acid, they were able to isolate the acid but considered it to be a 'keto a $\beta\beta$ tri methylglutaric acid, because they found that on heating it was converted into trimethylsuccinic anhydride with an evolution of carbon monoxide. They were, however, unable to definitely establish the ketonic character of the substance, for although they prepared derivatives by the action of hydroxlamine and parabromophenyl dydrazine, the compounds formed were ill defined and were not analysed. Balbiona on his final paper on the subject (*Berichte* 1897, XXX., 289) showed that the parabromophenylhydrazone of Mahla and Tiemann was in fact an addition product and not a hydrazone. In this paper he suggested that the compound had the oxide formula (I)



(1)



(2)

apparently forgetting his earlier work with *regard to a hydroxyl group in the molecule.* The formation of the acid from camphoric acid by oxidation appears reasonable on conventional lines, but the formula for *the acid is a peculiar one,* since it has no analogue among the acids of the glutaric series; also the formation of the oxide must *take place through the cis* or trans forms of the acid (2) by the elimination of water. There is ample evidence to show the manner in which the cis and trans forms of *dihydroxy acids of this type behave on dehydration.* because the cis and trans forms of bromolactone esters in the cyclohexane series have been proved by Ingold Beesley *and Thorpe to pass on treatment* with alkali through the corresponding dihydroxy acds to the cis and trans forms of the corresponding lactones. There is no evidence whatever to show any tendency exists to form butylene oxide rings by the elimination of water between the hydroxyl groups. *The production of an acid of the formula assigned* by Balbrona to his compound therefore appeared highly improbable. The keto formula (3) of Mahla and Tiemann *must next be considered and in the light of* what has been said. It might be expected to be a compound tautomeric with its hydroxy ring acid (4) (5), the tautomerism being of the types B and C.

$$CMe_2 < \begin{matrix} C(OH)CO_2H \\ | \\ CMeCO_2H \end{matrix} \rightleftarrows$$

(3)

$CO\ CO_2H$

CMe_2 $\rightleftarrows$

$CH\ Me\ CO_2H$

(4)

$C(OH)CO_2H$

CMe_2 O

$CH\ Me\ CO$

(5)

The main objection to this is that neither the tautomeric individual as (3) or (5) is capable of being represented as derived from camphoric acid by the elimination of water from the *aa* 'di hydroxy acid, but on the other hand the ring hydroxy acid can be represented as having been produced by dehydration of camphoric acid. The best *reagent for the characterisation of a keto ββ* dimethyl glutaric acid was found by Perkin and Thorpe to be orthotolylenediamine, which reacted in acetic acid solution to form a condensation product. A similar reaction was carried out by Thorpe, Kon and Stevenson with orthophenylene diamine and it was found that the dimethyl *acid condensation* product is rapidly and quantitatively precipitated when the reacting substances are warmed. The same is the case with the *other ketoglutaric acids discussed in their* paper (*Jour. Chem. Soc.* 1922, CXXI., 660) and it is worthy of note that ketoglutaric acid itself reacted in this way. When, *however,* the reaction was applied to Blabiona's compound, evidence was obtained of the tautomeric character of the compound. *When, for example, the acid* is treated with orthophenylenediamine in acetic acid solution, the condensation product is precipitated on boiling for a short time to the extent of 50 %, the *remainder* being a more soluble substance, an addition product which passes into the condensation product when heated above its melting *point, water being eliminated.* It can be shown to be an addition product by the fact *that its aqueous solution is acid* and this solution does not yield orthophenylenediamine when *made* alkaline, or, in other words, it is not a mere salt of acid and base. The formation of this addition product recalls the compounds obtained by Mahla and Tiemann by means of hydroxylamine and parabromo phenylhydrazine. Taken in conjunction with the formation of the condensation product of the keto acid, furnishes the strongest evidence for the tautomeric nature of Balbionos acid. The presence of the hydroxy phase is of course revealed by the formation of acetyl and benzoyl derivatives of the dimethyl compound described by Balbiona.

The alteration of the tetrahedral angle formed by two of the four valencies of a carbon atom has been shown to be affected firstly by the volumes of the groups attached to the valencies as calculated from a knowledge of atomic volumes, and secondly, by initial alteration in the angle of any two valencies by their participation *in a ring complex (loc cit).*

The earlier work, in connection with the effect of the experiments, were concerned with the gem dimethyl group, but it is clear that there is no reason why the other gem dialkyl groupings should not act in a manner similar to the dimethyl grouping, but modified to a certain extent.

The fact that the effect is a modified one is demonstrated by certain observations which have been recorded from time to time, thus, for instance, Freund and Fleischer (*Annalen* 1910, CCCLXXIII., 291) have shown that whereas diethylmalonyl chloride reacts with benzene to form six five bicyclic systems, the corresponding dimethyl compound cannot be made to form the indandione ring system. The search was made for a grouping which would make a substance, an open chain ketone enter into tautomeric equilibrium with its isomeric hydroxy ring compound, by the deflection of the tetrahedral angle such as to bring together the two carbon atoms attached to the valencies affected into suitable positions and exhibiting therefore tautomerism of the type C.

In the cyclohexane series, it will be recalled that the hydroxy ring acid is stable, for instance it is unaltered by aqueous alkali and is produced from the dibromo ester by means of strong potash. While, on the other hand, in the gem dimethyl series, the stable form, is the open chain keto acid, because this is not only unaltered by aqueous alkali, but when any attempt is made to produce the hydroxy ring acid by the action of strong alkali on the dibromo ester the product consists of the keto acid together with the ethoxy compound. The formation of these substances, clearly can only be explained on the assumption that the hydroxy ring acid is formed in the first place and then undergoes fission through the addition of either water or alcohol formed during the hydrolysis of the dibromo ester, this is supported by the fact that if alcoholic potash is employed, the sole product is the ethoxy compound. Since therefore we have in the gem dimethyl series conditions present which favour the formation of the open chain keto acid and in the cyclohexane series, conditions which favour the formation of the hydroxy ring acid, it is possible to visualise a molecular condition due to the deflection of the tetrahedral angle between these two extremes, in a system in which both the forms would be capable of existence namely, in which we have tautomeric equilibrium between the open chain keto form and the hydroxy ring form. The research of Deshapande and Thorpe (*Jour. Chem. Soc.* 1922, CXXI, 1432) has shown that the gem diethyl grouping produces the required deflection for ring chain tautomerism of the type cited above, and the substances (6) and (7) are tautomeric in the sense stated in this paper and we have an equilibrium mixture of the two forms.

$$(6)\quad Et_2C < \begin{matrix} CO\,CO_2H \\ CH_2CO_2H \end{matrix} \quad \rightleftarrows$$

$$Et_2C < \begin{matrix} CH\,CO_2H \\ | \\ C\,(OH)\,CO_2H \end{matrix} \quad (7)$$

The mixture contains approximately 38 % keto and 68 % hydroxy ring acid. The effect of the gem diethyl group as compared with the gem dimethyl group in deflecting the tetrahedral angle and thus increasing the ease of formation and stability of the cyclopropane ring is also apparent when the cis and trans forms of 3:3 diethylcyclopropane 1:2 dicarboxylic acid are compared with the corresponding members of the gem dimethyl series. For while in the gem series, fission occurs readily in the presence of mineral acids to yield terebic acid, the diethyl acids are quite unaltered even at high temperature by concentrated acids.

The substances used by Deshapande and Thorpe were obtained from $\beta\beta$ diethylglutaric acid which was obtained by Guareschi's method from diethyl ketone and ethyl cyanoacetate in the presence of ammonia; the acid was brominated and converted into the dibromo ester, from which the dibromo acid was obtained evidently in the cis form from which it was converted into the anhydride by means of acetyl chloride. The dibromo ester is capable of being distilled without decomposition into the bromo lactone ester and ethyl bromide. The ester therefore behaves like the corresponding dibromo ester in the dimethyl series and unlike the analogous ester in the cyclohexane series which cannot be distilled without undergoing change. This difference in behaviour has already been commented on in the case of the dibromo ester derived from cyclopentane (*Jour. Chem. Soc.* 1920, CXVII. 1582) which was found to behave like the corresponding ester in the dimethyl

series, despite its cyclic structure and high molecular weight. It is, however, difficult *to draw conclusions from a reaction such as* this where one has cis and trans forms, since one will be converted into the other during the course of distillation, and this complicates the issue, and one form will tend to split off ethyl bromide more readily than the other and the proportions in which the two occur in the original mixture are not subject to control. Nevertheless, on broad lines and eliminating as far as possible the variables, a reaction of this kind carried out with a substance of similar constitution, may be considered to afford valuable confirmatory evidence regarding the general structure, and in fact in the gem diethyl series the dibromo ester is stable, and falls into line with the general view that the *effect of two ethyl groups as compared with* two methyl groups not only leads to increased stability, but also affects the closing of the cyclopropane complex easier.

Highbury New Park,
N.5.

SODIUM TUNGSTATE.

BY EDGAR F. SMITH.

(Contribution from the John Harrison Laboratory of Chemistry—University of Pennsylvania.)

(*Continued from Page* 258).

In the present study the manganese, cobalt, strontium and cadmium precipitates from a *cold* solution of the sodium 5:12-salt, followed the ratio of the latter salt.

In the analytical work connected with this study as a rule, the Gibbs modified Berzelius method was adopted in determining the tungsten trioxide, and the sodium oxide, by difference, although quite often the analyses were conducted by the old Scheele procedure. Another scheme was found which proved good. It consisted, first in igniting, let us say, a gram of pure 5:12-salt. The loss sustained represented the water of the salt. The residue, or a portion of it, was next exposed in a porcelain boat to the hot vapours of pure carbon tetrachloride. This volatilized the tungsten trioxide, leaving sodium chloride, which was calculated into its equivalent of sodium oxide. The quantity of the latter deducted from the weight of anhydrous 5:12-salt gave the tungsten trioxide by difference. As examples of the accuracy of the procedure the following results are offered:

1. One gram of normal sodium tungstate was ignited to constant weight. The loss was 10.99%, whereas the two molecules of water required a loss of 10.91%. 0.3198 gram of the dehydrated salt gave 1.1277 grams of sodium chloride or 21.18% of sodium oxide, instead of the calculated 21.09% Na_2O. The tungstic oxide by difference equalled 78.82% instead of 78.91% by calculation.

2. Portions of the fused 5:12 salt gave

Na_2O	10.24%	10.07%	10.12%
WO_3	89.76%	89.93%	89.88%

while the calculated requirements were: 10.02% of Na_2O and 89.98% of WO_3.

3. Several weighed samples of dehydrated barium salt (5 BaO . 12 WO_3) were exposed to the action of the carbon tetrachloride vapours with these results:

WO_3	78.12%	78.40%
BaO	21.80%	21.60%

while the calculated percentages of 5 BaO . 12 WO_3 are

BaO	21.55%
WO_3	78.45%

A portion was also subjected to decomposition with hydrochloric acid, weighing the separated tungstic oxide, and estimating the barium in the form of its sulphate.

	Found
Ba%	21.61%
WO_3	78.39%

Omitting other similar results, the scheme proved most helpful and may be depended upon. It shortens the customary procedure very much.

SUMMARY.

The study set forth in the preceding paragraphs follows in this summary:

1. The absolute conditions to be observed in getting 5:12-sodium tungstate have been determined.
2. With normal sodium tungstate (1:1) and meta-sodium tungstate (1:4) as opposites in basic and acid character, the intermediates 3:7, 5:12 and 4:10 *have been found* as products of their *union*. This fact has been proved by analysis of the fused intermediates, by their hydrolysis, and by their synthesis.
3. The 1:2 and 1:3-sodium salts do not

exist, because very probably of their ready hydrolysis.

4. The 3:7-sodium salt of Marignac does exist. It was synthesized.
5. von Knorre's suggestion that paratungstates might exist in two modifications, viz. 3:7 and 5:12, is not justified. His 3:7 derivatives were a consequence of the hydrolysis of 5:12 bodies.
6. Carbon tetrachloride has been found to be a new and valuable reagent in the analysis of tungstates, and was much resorted to in the more than seven hundred distinct determinations made in the course of the present investigation.

This study has been possible through the gracious aid of the Carnegie Institution in Washington, and for this aid thanks are here made.

To Russell Davis and Julie Bodle for their hearty co-operation and assistance, the writer acknowledges his sincere gratitude.

GENERAL NOTES.

FREE PASSAGES TO AUSTRALIA AND NEW ZEALAND FOR UNIVERSITY GRADUATES.

GENEROUS POLICY OF STEAMSHIP COMPANIES.

The six great lines engaged in the passenger service to Australia and New Zealand have agreed to grant eight free first-class return tickets, yearly, to University graduates desirous of studying problems connected with the development of the resources of the Dominions, or of holding temporary teaching posts. The selection of the recipients is to rest with a committee of the Universities Bureau of the British Empire.

SUGAR MIXTURES:

SUCROSE, INVERT SUGAR, AND WATER.

The solubility of sucrose in the presence of invert sugar has been studied by Prinsen Geerligs. From a series of measurements, in which sucrose was dissolved in the presence of invert sugar to form supersaturated solutions and subsequently allowed to crystallize, he drew the conclusion that the presence of invert sugar was without influence upon the solubility of sucrose. Since the solutions upon which he experimented remained motionless during the crystallization, it is probable that they were supersaturated even at the end of one month, the time allowed by Geerligs.

A portion of our measurements on this system was made in 1917. The work was then interrupted and the results were withheld from a more general publication because they were not satisfactorily complete. In the meantime, van der Linden has published his measurements on this system. As will be observed from Figure 2, the two sets of measurements are in approximate agreement.

For the experiments described below the invert sugar was prepared from pure sucrose either by inversion with a minute quantity of hydrochloric acid which was subsequently neutralized or by use of a small quantity of invertase. After completion of the latter inversion the solution was heated to 70 or 80° C. in order to inactivate the enzyme.

Dept. of Commerce, U.S.A.

COMMERCE AND INDUSTRY IN GERMANY DURING SEPTEMBER.

The Commercial Secretary at Berlin (Mr. J. W. F. Thelwall) has forwarded to the Department of Overseas Trade the following review based on the Reports of the Prussian Chambers of Commerce of the trade and industry of Germany during September, 1924.

The economic situation showed a small improvement in September, particularly in the case of the mining, potash, and textile industries, and certain branches of the food industry. In the iron industry there was slightly more activity at the beginning of the month, owing evidently to the acceptance of the London Agreement, but towards the end of the month this activity again declined. In general, the hopes attached in many quarters to the London Agreement have not yet materialised. This was, however, scarcely possibly, as neither the political nor the economic effects of the Agreement are yet fully discernable. The firmer tone on the Stock Exchange was maintained, but did not become "bullish."

MINING INDUSTRY.

A very slight improvement set in in Sep-

tember in the Westphalian mining industry. Although the market crisis still continued, sales increased to a small extent, and a further increase is anticipated as a result of the reduction in the prices of coal on the 1st October. It is, however, an essential condition of any permanent improvement that coal freights should be further reduced, in particular that preferential tariffs should be introduced for coal consignments to the German North Sea ports, and that the water transhipment tariffs and coal freights to Holland and Switzerland should be extended. The coal output increased not inconsiderably. The daily production rose from 285,444 tons in August by about 18,000 to 303,397 tons in September. The effect of the slight improvement in sales was seen in the important reduction in the number of dropped shifts. In about 270 cases approximately 325,000 miners were effected by idle shifts; that means a reduction of more than 50% as compared with the previous month. The deficit in output may be estimated at about 280,000 tons and the decrease in wages at about 2 million marks.

Potash.

In the potash industry there was an important increase both in inland and foreign sales. The reinstatement of workmen who had been previously dismissed was possible in individual works.

Iron Industry.

After the acceptance of the London Agreement by the Reichstag, the arrangements made thereunder came into force. The apparent revival of the market after such acceptance was of only short duration and has given way to almost complete stag- the mar- nation. The present dullness of ket is partly due to the anticipation of buyers of a further fall in prices as a result of the reduction of freights and the pending decrease of coal prices etc. Above all, press reports in regard to proposed action by the Government with a view to lowering prices have contributed towards bringing the market to a complete standstill.

Electro-Technical Industry.

In this industry the slight improvement which set in in August was maintained in September. There was everywhere a demand, and only the exceptional shortage of money hindered the placing of new orders. As regards the individual branches of the industry, business in power plant improved. In the telegraphy and telephony branch orders increased somewhat. Business in automatic telephone apparatus continued to make good progress. The factories manufacturing electro-medical apparatus were better employed. Orders for fittings for tramcars increased, while those for electric full gauze railways were satisfactory. The turnover in incandescent lamps was greater than in the preceding quarter but smaller than in the corresponding period of last year.

Chemical Industry.

There was no change of any importance in the situation of the chemical industry. Sales of fertilisers have increased. In the dye industry the market possibilities continue unsatisfactory. Bnsiness in glass chemicals improved slightly, while only a few orders for laboratory chemicals were received. Scientific institutions lack just as much as the large industrial laboratories the requisite money for covering their most urgent requirements.

UNITED STATES BUSINESS CONDITIONS.

The Representative in London of the Irving Bank-Columbia Trust Company, New York, has received a cable from headquarters stating that silk consumption during September amounted to 36,36(bales, the highest since April, 1923. Pig iron output last month totalled 2,053,00(tons, and steel ignot production 2,670,00(tons. The general business situation is im proving, while in building the tendency i firm.

RIO DE JANEIRO OILS CONGRESS.

The Commercial Secretary at Rio d Janeiro has forwarded a copy of the advanc programme (in Portuguese) of the Oils Cor gress to be held in Rio de Janeiro from 15t to 22nd November, 1924. He states tha is the first Conference of its kind to be hel in Brazil, and that the importance to Braz of this branch of production is now though to be more widely recognised.

The advance programme referred to ca be consulted by British firms interested o application to the Department of Oversee Trade, 35, Old Queen Street, Londor S.W.1.

JAPAN AFTER THE EARTHQUAKE-FIRES.

In the course of a Report on the Economic Situation is Japan, Mr. G. B. Sansom, Acting Commercial Counseller in Tokio (assisted by Mr. W. J. Davies, Acting Commercial Secretary), gives an account of the earthquake-fire damage in September, 1923, and of the measures taken by the Japanese Government to meet the emergency and to reconstruct the devastated cities. Mr. Sansom also discussed the stagnation of Japan's export trade.

BRITISH TRADE WITH THE ARGENTINE.

The Journal of the British Chamber of Commerce to Argentina says:—

British trade with Argentina has been well to the fore for more than 100 years, ever since our country led the van by being the first of the Powers to recognise the young Republic after she broke with Spain and declared her independence in 1810, and no Britain must allow himself or herself to doubt that we shall retain and improve our position.

But to those of us who live in Argentina it sometimes seems that you at home fail to appreciate the danger of growing competition by rivals all over the world. It is impossible within the limits of this article to examine in detail the many possibilities of British trade, but the following outline may be found interesting.

Chemicals and Drugs. In these lines the United States, as well as European Continental competitors, dispute the field with us. During the last three or four years large quantities of coarse chemicals, such as chloride of calcium, chloride or barium, sulphate of copper, and silicate of soda, have been sent from Germany to Argentina oking to lower f.o.b. prices, combined with lower freight rates, than when obtainable from Great Britain. Again, fine chemicals are now supplied in large quantities by Germany as before the war.

THE ROYAL COMMERCIAL TRAVELLERS' SCHOOLS.

These Schools, which were established at Wanstead in 1847 and eight years later at Pinner, for the orphan and necessitous children of Commercial Travellers, have continued every year to expand and develop their work and interests to meet modern requirements, and to-day they stand in the front rank of institutions of their kind.

The Board of Management is comprised mainly of heads of firms whose names are household words in the commercial world. Mr. Howard Williams is the Chairman, Sir Jeremiah Colman, Bart., Sir Charles C. Wakefield, Bart., and the Hon. Geoffrey Hope Morley are the Trustees. The President of the 79th Festival, which will be held in London shortly, is Mr. Geo. W. Paton, Chairman and Managing Director of Messrs. Bryant & May, Ltd., and the Secretary of the Schools, by whom any information will be gladly given, is Mr. W. P. Leas, 17, Cheapside, E.C.2.

SOUTH AFRICAN DEPARTMENT OF AGRICULTURE.

The many activities of the above must play a prominent part in increasing the health and prosperity of the inhabitants. A few samples of these activities will be interesting.

Calcium Synanide for Moles.—For some time past the Eastern Province Entomologist, Mr. D. Gunn, has been supervising the control of the golden mole and mole rats inhabiting the rough ground beyond the fairways of the Port Eliabeth golf links. During June last, Mr. Gunn treated over forty burrows with calcium cyanide, and since then none of the treated burrows nor those in their immediate vicinity have been reopened. Other burrows were treated with liquid cyanide, but these in many cases have had to be retreated. It would, therefore, appear that the calcium cyanide is much more effective. Earlier treatments with calcium cyanide conducted in November, 1923, were equally successful as for over nine months none of these had been reopened. The cost of treating a burrow with calcium cyanide worked out, with railage and other charges, at twopence per burrow, whilst the less satisfactory liquid cyanide cost sixpence. The effectiveness of the calcium cyanide is thought to be due to the slow evolution of the gas.

Larkspurs and Locusts. Several correspondents have recently observed the poisonous effect of larkspurs and delphiniums on

locusts. One at the Crown Mines, wrote to say that after the locusts had fed a little on larkspurs the insects "fell over and died." Last summer a cotton grower in Zululand found that the elegant grasshoppers feeding on delphiniums sickened and died. Another writes:—

"It has just come to our notice from one of our clients who is farming in the Brits District, that his entire crop of flowers has been destroyed by locusts. It may be of interest to you to know that the locusts have not destroyed the fields of delphiniums, and wherever they have nibbled the flowers they have died by the millions."

These observation are quite in keeping with the well-known toxic effect of the plants, and to which there are many references in literature extending back for forty years on more. In their young stages of growth certain of the larkspurs are stock poisons and powdered seeds, and decoctions have been frequently recommended as insecticides, but larkspur poison has never come into the front rank as an insecticide.

THE GROWTH OF THE CANADIAN INSTITUTE OF CHEMISTRY.

The Canadian Institute of Chemistry has just issued its second publication, containing revised by-laws, a code of professional ethics, and a very representative list of members.

The qualifications for admission have been raised, particularly for the Fellowship, and, while not beyond a reasonable standard, are hardly subject to criticism on the ground that anyone is likely to become a member without demonstrating real capacity as a chemist.

University degrees are granted, in general, because individuals give promise, through their scholastic ability, or their early experimental work, that they may be entrusted with the control of serious chemical matters. The Institute takes up where educational institutions leave off, and endeavours to give all Canadian chemists a more general professional standing, based on actual attainment. A glance through the list just issued shows that many of the leading university and industrial chemists in all lines have joined forces, to work out the ever-changing general situation that faces their particular profession.

Even yet, the conception of Chemistry as a profession is strange to some chemists, Some attempt to circumvent their special field with high boundaries, creating a type of specialization which may shut out more avenues of development than are enclosed.

But these are in the minority. The majority of Canadian chemists have set themselves to the main task, which involves the placing of the chemical profession on a higher level of quality, and the creation of something that will be tangible, in a national way, and will be expressed in terms that non-chemists can appreciate and evaluate properly. This accomplished many of the individual ills of chemists should cease to annoy, and the exercise of doing the thing will stimulate a much-needed confidence and pride in professional chemical attainments, as an equipment for successful lifework.

THE ATOMIC WEIGHTS.

By A. W. Warrington.

In November, 1914, while I was in the interior of China, and unaware of Moseley's work on the X-ray spectra of successive elements, I became convinced that the atomic weights were a function of the square of the atomic number, and that the number of elements was limited. In an article, which appeared in *The Chemical News* (March 5, 1915), I suggested that only eighty-five elements existed between hydrogen and uranium. As we now know, this estimate was short by five, but I cannot help thinking that there must have been some justification for the reasoning which led me to make the suggestion.

With the new data in my possession I have found that the approximate atomic weight of an element can be found from the following formula:

$$A = 2N + 0.00678 N^2$$

in which N is the atomic number.

In the table column 2 contains the accepted atomic weights, and column 3 those calculated from the above formula. The differences between the observed and calculated do not give the signs evenly distributed, but the figures do suggest that there are definite limits within which the mass of the nucleus must be confined if it is to remain stable with a given number of electrons.

It would be easy to invent other formulae to give more correct figures for ele-

ments with low atomic weights. For example—

$$A = 2N + \frac{(N - 7^2 (N + 1029)}{976.5 \quad (N + 60.75)}$$

But all attempts to do more than show that the atomic weight has a value which depends on the square of the atomic number are futile, until more is known of the effects on the weight of the nucleus produced by the introduction of new groups of electrons.

If N is the atomic number of an element, and v the vibration frequency of the principal line in the Xray spectrum, whilst A is a constant, the following relationship holds:

$$v = A(N - 1)^2$$

The formula I have sent you can easily be transposed into the following

$$A - 2N = 0.007(N - 1)^2$$

in which A is the atomic weight and N the atomic number.

The similarity of the two formulae is striking.

Of course my formula has the objection advanced against the periodic arrangement of the elements according to their atomic weights, it would still place A after K, etc.

Atomic Weights.

		Calc.	Diff.			Calc.	Diff.
H	1	2	-1.0	Ru	101.7	101.1	+0.6
He	4	4	0.0	Rh	102.9	103.7	-0.8
Li	6.9	6.1	+0.8	Pd	106.7	106.3	+0.4
Be	9.1	8.1	+1.0	Ag	107.9	109.0	-1.1
B	10.9	10.2	+0.7	Cd	112.4	111.6	+0.8
C	12	12.2	-0.2	In	114.8	114.3	+0.5
N	14	14.3	-0.3	Sn	118.7	117.0	+1.7
O	16	16.4	-0.4	Sb	120.2	119.6	+0.6
F	19	18.6	+0.4	Te	127.5	122.3	+5.2
Ne	20.2	20.7	-0.5	I	126.9	125.0	+1.9
Na	23	22.8	+0.2	Xe	130.2	127.8	+2.4
Mg	24.3	25.0	-0.7	Cs	132.8	130.5	+2.3
Al	27.1	27.1	0.0	Ba	137.4	133.3	+4.1
Si	28.3	29.3	-1.0	La	139.0	136.0	+3.0
P	31	31.5	-0.5	Ce	140.3	138.8	+1.5
S	32.1	33.7	-1.6	Pr	140.9	141.6	-0.7
Cl	35.5	36.0	-0.5	Nd	144.3	144.4	-0.1
A	39.9	38.2	-1.7	Sa	150.4	150.1	+0.3
K	39.1	40.4	-1.3	Eu	152.0	152.9	-0.9
Ca	40.1	42.7	-2.6	Gd	157.3	155.8	+1.5
Sc	45.1	45.0	+0.1	Tb	159.2	158.6	+0.6
Ti	48.1	47.3	+0.8	Dy	162.5	161.5	+1.0
V	51	49.6	+1.4	Ho	163.5	164.4	-0.9
Cr	52	51.9	+0.1	Er	167.7	167.4	+0.3
Mn	54.9	54.2	+0.7	Tm	168.5	170.3	-1.8
Fe	55.8	56.6	-0.8	Yb	173.5	173.2	+0.3
Co	59.0	58.9	+0.1	Lu	175	176.2	-1.2
Ni	58.7	61.3	-2.6	Ta	181.5	182.1	-0.6
Cu	63.6	63.7	-0.1	W	184	185.1	-1.1
Zn	65.4	66.1	-0.7	Os	190.9	191.2	-0.3
Ga	70.1	68.5	+1.6	Ir	193.1	194.2	-2.1
Ge	72.5	70.9	+1.6	Pt	195.2	197.3	-2.1
As	75	73.4	+1.6	Au	197.2	200.3	-3.1
Se	79.2	75.8	+3.4	Hg	200.6	203.4	-2.8
Br	79.9	78.3	+1.6	Tl	204	206.5	-2.5
Kr	82.9	80.8	+2.1	Pb	207.2	209.6	-2.4
Rb	85.5	83.3	+2.2	Bi	208	212.7	-4.7
Sr	87.6	85.8	+1.8	Nt	222.4	222.1	+0.3
Y	89.3	88.3	+1.0	Ra	226.0	228.5	-2.5
Zr	90.6	90.8	-0.2	Th	232.2	234.9	-2.7
Nb	93.1	93.4	-0.3	U	238.2	241.4	-3.2
Mo	96	96	0.0				

PROCEEDINGS AND NOTICES OF SOCIETIES.

INSTITUTE OF MINING ENGINEERS.

PRESIDENTAL ADDRESS.

THE VALUES FOR WHICH THE INSTITUTION STANDS.

(*Continued from Page 280*).

My own work in pure science can be summed up in the conclusion that the mechanical conceptions of physical science break down irretrievably when we endeavour to apply them to life and conscious behaviour, both of which are just a part of what we call Nature. We cannot in the long-run dispense with the spiritual conception of Nature; and I have just tried to point out that the mere economic conception of industrial life breaks down equally hopelessly when we try to apply it to such an industrial undertaking as a British coal-mine. The mere physical and economic conception of reality seems to leave us with a conscious life made up of grim experience, variegated by passing sensations and thrills such as those of interior cinemas, sensational literature and newspapers, and windy oratory, forgotten next day. Such a conscious life is nothing but that of a degenerate. The more earnest-minded men who accept the supposed realism, but rightly despise the world it represents, are, it seems to me, the real moving spirits in labour unrest; and they are striving after what seems to us to be Utopias. Where they really fail, however, is in not seeing to what an extent there is aleady a spiritual world around them, realized in the comradeship of daily life.

It appears to me that though we may differ from these men as regards the means, we are on common ground with them as regards the real ends in view, and that there is no reason why we should not work alongside of them over many matters that both we and they have at heart. As regards workmen's organizations, I think we should all go much farther than this: for through their agency much has been done for the good of the mining industry, and the country as a whole, which never could have been done without them. It is impossible to give effective help to people who do not help themselves; but apart from this, it is both the right and the duty of all connected with the mining industry to contribute such constructive ideas and actions as they can. When these ideas and actions are contributed in the spirit of comradeship, we can receive them in the same spirit; but when they are contributed in that spirit, then we must fight them as we fight deleterious gases, coal-dust, gob-fires, falls of roof, water, failing markets, and all the other troubles and danger of mining work.

If at any time we feel discouraged, we should remember that behind our comradeship there stands the wider comradeship of which the British Flag is for us the symbol —a symbol alike of righteous and humane dealing, and of the fearless power that lies behind it. Let us never allow the fickle waves of passing public sentiment to obscure our vision of that wider comradeship.

I think I have now said enough to make my main point clear. It is that whatever may be the immediately apparent values for which this Institution stands, they are, in reality, spiritual values. The spiritual values include, and at the same time transform, the apparent values.

It is not my business to preach a sermon: I am only trying to help you to understand our position. What I have said is based on long observation of the Institution and its members. My memories of it go back to many of those who are no longer with us, and in writing this address, I have had them ever in mind. They brought with them to our meetings the comradeship of British pitmen. It seemed to shine in their faces and sound in their voices and be carried in the shake of their hands. We can read the *Transactions* at home; but something more subtle than print can convey is conveyed to us at our meetings and dinners.

This Institution has grown from the comradeship of British mining engineers as British pitmen; it stands for that comradeship, and I am convinced that so long as it exists it will continue so to stand.

ROYAL MICROSCOPICAL SOCIETY.

An interesting programme for the 1924-1925 Session has been issued. The various meetings are to be held at 20, Hanover Square, London, W.1. The Session opened with a series of papers on October 15th, followed on October 22nd by a meeting of the *Industrial Applications Section*. On November 19th papers are to be read by Mr. G. R. De Beer, B.A., B.Sc. (Merton College, Oxford) on " Comparative Histology and

Cytology of the Pituitary Body," while Miss J. Latter, B.Sc., is to read a paper on "Pollen Development in Lathyrus."

THE CHEMICAL SOCIETY.

ORDINARY SCIENTIFIC MEETING, THURSDAY, NOVEMBER 6TH, 1924, AT 8 P.M.

The following papers will be read: —

"Investigations on the Dependence of Rotary Power on Chemical Constitution. Part XXIV. Further Experiments on the Walden Inversion," by J. Kenyon, H. Phillips and H. G. Turley.

"Studies of Valency. Part V. The Mechanism of the Walden Inversion," by T. M. Lowry.

"*A Spectroscopic Study of the Luminescent* Oxidation of Phosphorus," by H. J. Emeléus and W. E. Downey.

INSTITUTE OF METALS.

LONDON LOCAL SECTION.

A Meeting will be held at the Royal School of Mines, South Kensington, on Thursday, November 13th, at 8 p.m., when Professor T. TURNER, M.Sc., A.R.S.M., F.I.C., President Institute of Metals, will give an address on "Oxidation, with special reference to Thin Films." All interested are invited.

ROYAL SOCIETY OF EDINBURGH—OFFICE BEARERS.

The Statutory Meeting was held on October 28th, at which the Office Bearers and Council as appended were elected:—

President.—Principal Sir James Alfred Ewing.

Vice-Presidents.—Principal James Colquhoun Irvine, Lord Salvesen, Professor J. H. Ashworth, Professor T. H. Beare, Dr. Walter Biggar Blaikie, Sir Robert Blyth Greig.

General Secretary. — Professor R. A. Sampson.

Secretaries to Ordinary Meetings.—Dr. Alexander Lauder, Professor W. Wright Smith.

Treasurer.—Dr. James Currie.

Curator of Library and Museum.—Dr. A. Crichton Mitchell.

Councillors. — Professor Thomas H. Bryce, Professor J. Y. Simpson, Professor D'Arcy W. Thompson, Professor Sir James Walker, Professor E. T. Whittaker, Professor Henry Briggs, Mr. W. L. Calderwood, Professor T. J. Jehu, Professor C. G. Barkla, Professor J. Graham Kerr, Lieutenant-Colonel A. G. McKendrick, Mr. James Watt.

SOCIETY OF APOTHECARIES—SUCCESSFUL CANDIDATES.

The following candidates were successful in the subjects named:—

Surgery. Bland, J. O. W., St. George's Hosp.; Hottinger, E. F., St. Mary's Hosp.; Jaecques, W. R. S., Ghent; McGuire, J. P., St. Mary's Hosp.; Moody, A. J., St. Bartholomew's Hosp.; Moody, C. M., St. Mary's Hosp.; Pennington, W. E., Liverpool; Rozario, C. J., St. Thomas's Hosp.

Medicine. Barnstein, H. L., Guy's Hosp.; Bland, J. O. W., St. George's Hosp.; Htoe, L. K., London Hosp.; Jones, R. D., Edinburgh and Middlesex Hosp.; Schofield, R., Guy's Hosp.

Forensic Medicine. Kaplan, A., St. Mary's Hosp.

Midwifery. Davies, T. G. L., St. George's Hosp.; Francis, B. M., Guy's Hosp.; Htoe, L. K., London Hosp.; Mellows, P. B. P., St. Bartholomew's Hosp.; Moody, C. M., St. Mary's Hosp.; Osbourne, A. B., St. Mary's Hosp.; Perott, B. A., Petrograd; Rozario, C. J., St. Thomas's Hosp.; Samaan, K., Cairo and Manchester.

The Diploma of the Society was granted to the following candidates entitling them *to practise Medicine, Surgery, and Midwifery*:—H. L. Barnstein, J. O. W. Bland, L. K. Htoe, W. R. S. Jaecques, R. D. Jones, W. E. Pennington, and R. Schofield.

MINERALOGICAL SOCIETY.

ANNIVERSARY MEETING NOV. 4.

Papers read:—

Dr. M. S. Krishnan: Note on Cordierite in a cordierite-gneiss from Madura district, Madras, India.

Dr. A. Brammall: Lime as a constituent of certain important rock-forming minerals: *its behaviour relative to that of other bases* of RO type.

A. Russell: A notice of the occurrence of native arsenic in Cornwall (with analysis by

Dr. H. F. Harwood); of bismuthinite at Shap, Westmorland; and of smaltite and niccolite at the Coniston Mine, Lancashire.

Dr. L. J. Spencer: An inclusion of magnetic in diamond.

Dr. L. J. Spencer: Biographical notices of mineralogists recently deceased (Second Series).

THE INSTITUTE OF PETROLEUM TECHNOLOGISTS.

Recent Development in the Art of Cracking.

By A. E. Dunstan and Robert Pilkethley (Members).

The thermolysis of the heavy oil is carried out in three distinct stages, which in effect are zones of temperature and rate of flow. In the first or preheating stage the oil is carefully heated to a point, preferably not more than 25° C. below what we defined as its " Optimum temperature," which is the temperature at which the specific extent of decomposition occurs, once the molecular inertia has been overcome. In this stage the rate of flow is immaterial, and the preheater can be of any form compatible with efficient temperature control.

In the second stage the oil is quickly raised to a temperature about twenty degrees above the optimum. This stage is very important and must be carefully controlled. It is here that advantage is taken of the time lag to give the oil its impetus towards disruption without materially effecting decomposition. This portion of the plant, termed the " Thermolyser," consists of a single pipe or a number of pipes in parallel of such a bore that the oil can be rapidly heated throughout its bulk, and of such a length that the oil has passed through with minimum amount of actual decomposition, or, at any rate, of separation of carbon.

After leaving the thermolyser the oil passes forthwith to the " Reactor." This is a vessel of such dimensions that in passing through it the oil remains for at least the amount of time necesssary to obtain equilibrium as regards the specific extent of decomposition required. By suitable means the reactor is maintained at or above optimum temperature. Owing to the endothermic nature of the reactions involved a certain amount of external heat must be supplied to do this. The position of the reactor is determined by the need of avoiding gas locks and shape by the accessibility necessary for cleaning. Since most of the carbon is actually formed in the reactor, and since it is of considerable size and the oil in it fairly quiescent, the bulk of the carbon produced in the process is deposited here. The cracked oil is drawn from the highest point of the reactor, condensed or dephlegmated, and discharged into a gas separator.

This plant has successfully cracked kerosene, gas oil, Scottish shale oil, paraffin sweats, Persian and Mexican fuels, but like other plants, it will not give a high yield of spirit from heavy residues and at the same time run for an indefinite period. The length of time it can operate is limited by the size of the reactor.

Yields of light spirit can readily be obtained varying from 10 to 30 per cent. Heavy residues which will not pass the Admiralty fuel test may be processed, producing a limited quantity of spirit and a liquid fuel which does not gel on standing for a considerable time.

CORRESPONDENCE.

To the Editor of The Chemical News.

Sir,—In a recent number of *The Chemical News* (1924, CXXVIII, 357) Dr. Heyrovsky has replied to the writer's criticisms of his paper, " The Significance of the Electrode Potential " (*Proc. Roy. Soc.*, 1923 [A], CII., 628) which appeared elsewhere (*ibid.*, CIV., 667). Since the arguments advanced do not by any means dispose of the question, I trust that you will allow me to make the following comments.

In the first place, in reply to my first criticism that free energy and total energy terms were used indiscriminately, Dr. Heyrovsky insists that all his energy and work terms are to be interpreted as free energy and maximum work terms corresponding to conducting every step reversibly. Dr. Heyrovsky employed energy and work terms without qualification in this respect, and my first criticism was based on their interpretation in the usual physical sense. It is certainly possible to make the interpretation which Dr. Heyrovsky desires,

though with some violence to the accepted usage in certain cases. For example, the statement is made in the original paper that "to replace the electrons into the metal requires work $-\Phi F + \phi - RT \log p$, where Φ denotes the energy of evaporation of "electron gas" from platitum to unit pressure." If Dr. Heyrovsky intended ΦF to be taken as the maximum work obtainable from the evaporation at unit pressure, which is simply RT provided the equilibrium P.D. is maintained throughout, and not as the latent heat of evaporation of electrons in the usual sense, he can scarcely complain of the validity of his argument is questioned.

But even accepting Heyrovsky's explanation that his energy terms are to be interpreted as free energies, his objection to the proof given that the sum of the amounts of maximum work obtainable in going round the cycle is zero does not hold good. In this proof it was assumed that if we have a solid metal in contact with its aqueous solution, the vapour phase above the solution may contain in addition to H_2O, the cons Me°, H° and OH' and free electrons E, in equilibrium with each other according to *the equations*

$$Me^{+} + \epsilon = Me,$$
$$Me^{+} + OH' = MeOH,$$
$$H^{+} + OH' = H_2O;$$

and in equilibrium with solid metal and the

$$\begin{array}{lcl} & \left.\begin{array}{l} Me\epsilon = Me^{+} + \epsilon \\ MeOH = Me^{+} + OH' \\ H_2O = H^\circ + OH \end{array}\right\} \text{Vapour phase} & \\ Me\,\epsilon & \overline{\hspace{12em}} & MeX \\ & \begin{array}{c} MeOH \\ \text{in } H_2O \\ \text{I.} \end{array} & \end{array}$$

Finally, I am quite unable to understand the arguments of the final "disclosure." Dr. Heyrovsky accepts the author's equation

$$\pi + E_s - \Phi_M = \frac{RT}{F} \log K_{Me} - \frac{RT}{F} \log K_{MeOH}$$
$$+ \frac{RT}{F} \log K_{H_2O} - \frac{RT}{R} \log \frac{pP}{(\epsilon_{In}\ H^\circ{}_s\ MeOH_s}$$

and attempts to deduce his own by the introduction of another quantity E, given by

$$E = -\pi + \Phi_m - E_s - \frac{RT}{F} \log (\text{-} + \text{const.}$$

aqueous solution a tone and the same time. Dr. Heyrovsky objects that the concentration of metal ions in equilibrium with the solid metal (Me^{+}_{e}) is not necessarily the same as that in equilibrium with the solution (Me^{+}_{s}) and to assume that they are the same introduces a new condition. The flaw in this argument is that there is *no unique condition of equilibrium of ions between two phases*. Just as a metal can exist in equilibrium with solutions containing different concentrations of its ions, so may it be equilibrium with a vapour phase containing its ions in varying concentrations. The P.D. at the interface adjusts itself so as to preserve equilibrium.

That the whole ensemble of equilibria is possible may perhaps be easiest shown by reference to an analogous and more familiar case. Instead of the metal $Me\,\epsilon$ we consider a salt MeX in which the ionizeable electron is replaced by a negative ion. Consider the equilibrium of such a salt with an aqueous solution of MeOH and with a second solvent B immiscible with water, containing perhaps a certain amount of water in solution and MeOH in accordance with the distribution colfficient. No one would suggest that the metal ion concen*tration in B could not be in equilibrium* with solid salt and with the acqueous solution at the same time. If now the solubility of the salt in the aqueous solution is negligible, the case is entirely analogous with *the one under discussion. (I. and II.).*

$$\begin{array}{c} \left.\begin{array}{l} MeX = Me^{+} + X' \\ MeOH = Me^{+} + OH' \\ H_2O = H^{+} + OH' \end{array}\right\} \text{in B.} \\ \overline{\hspace{14em}} \\ \begin{array}{c} MeOH \\ \text{in } H_2O \\ \text{II.} \end{array} \end{array}$$

He thus obtains

$$E = K - \frac{RT}{F} \log p + I - M + \frac{RT}{F} \log \frac{C_{MeOH}}{C_{OH}} - H_{MeOH}.$$

An equation whose "identity" with his original equation for the electrode potential π

$$\pi = K - \frac{RT}{F} \log p + I - M + \frac{RT}{F} \log \frac{C_{MeOH}}{C_{OH}} - H_{MeOH}$$

he acclaims as a further proof of the correctness of the latter!

I am, Sir,
Yours, etc.,
J. A. V. BUTLER.

Chemistry Department,
University College of Swansea.

AN ATOMIC COMPONENT OF ZERO VOLUME?

To the Editor of THE CHEMICAL NEWS.

Sir,—Referring to your issue of October 10th, p. 222, it would appear from Mr. Collins' method of breaking up the atom into component parts, having different volumes according to the compound in which the element enters, that in some cases the volume is zero. If, for example, silver of atomic volume 9.78 consists of C vol. 0.71 + Cu vol. 9.07 + S vol. 0.0, then one component element has disappeared entirely, for how can it be a part and yet have no volume. Perhaps Mr. Collins will explain this paradox.

Yours etc.,
F. H. LORING.

BOOKS RECEIVED.

Qualitative and Volumetric Analysis, by WILLIAM COLDWELL, M.A., Sc.D. xxiv. + 418. London: J. & A. Churchill, Great Marlborough Street. 1924. 10s. 6d. net.

Quantitative Organic Microanalysis, by FRITZ PREGL, Ph.D. Translated from the second German Edition by E. FYLEMAN, B.Sc., Ph.D., F.I.C. xv. + 190. London: J. & A. Churchill, 7, Great Marlborough Street, W.1. 1924. 12s. 6d. net.

The classical methods of elementary organic analysis have undergone little change since the time of Liebig, Dumar and Carius. The ordinary combustion processes still require from 0.5—1.0 gr. for reliance to be placed in the analytical results. By Prof. Pregl's methods, *12 to 15 milligrams* suffice for ordinary purposes, and with double this amount a molecular weight determination may be carried out.

The tremendous importance of this process needs no emphasis. This influence of traces of substances is now realised in all branches of chemical science. By the appearance of this translation, well-tried quantitative micro-analytical methods are brought to the notice of analysts in this country. Small amounts of foreign substances in industrial products may be subjected to a complete analysis—a process previously impossible.

Detailed directions are given of the methods described, and a list of researches in this field is given towards the end of the volume. On page 186 there is a list of continental firms who make and supply the various pieces of apparatus described. If the demand arose, there seems no reason why some of these at least should not be made in England.

The Extra-Pharmacopoeia, by W. H. MARTINDALE, Ph.D. and W. WYNN WESTCOTT, M.B., DP.H. 18th edition. Vol. 1. Pp. xxxviii. + 1163. London: H. K. Lewis. 1924. 27s. 6d.

The Extra-Pharmacopoeia needs no introduction to pharmacists and druggists or to the medical profession. It has established itself as one of the standard works of reference since its first appearance in 1883. The amount of material that has been compressed into this volume is truly amazing. Among the additions made in the latest edition, mention may be made of the following subjects:—The substitution of isopropyl alcohol for ethyl alcohol in certain preparations; the use of metals in the colloidal state; hypochlorous acid and hypochlorites; new arsenicals and antimonials.

The Extra-Pharmacopoeia is an indispensable volume to pharmacist and druggist. Analysts and other concerned with the making and use of pharmaceutical preparations cannot afford to ignore this well-known guide.

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

24377—Haco-Ges Akt. Ges. Bern.—Manufacture of compounds of alkaloids. Oct. 14.

Abstract Published This Week.

221008—Perylene derivatives. — Kalle & Co., Akt-Ges, 23, Rheinstrasse, Biebrich-on-Rhine, Germany.

3:4:9:10-*Perylene tetracarboxylic acid, its halogenated derivatives and the corresponding monoimides and anhydrides* are prepared by hydrolysing with strong or fuming sulphuric acid the di-imides thereof, that is, the colouring matters obtainable by alkali fusion of naphthalene-1:2-dicarboxylic imide or its halogen derivatives; at high temperatures the acids are obtained, at lower temperatures the mono-imides which, by further hydrolysis also yield the acids. The following examples are given:—(1) the di-imide of perylene tetracarboxylic acid (obtained by alkali fusion of naphthalene-1:8-dicarboxylic imine as described in example 1 of Specification 26690/13) is converted by heating with concentrated sulphuric acid at 180° C. into a mixture of the monoimide and the tetracarboxylic anhydride; they may be separated by taking advantage of the differing solubilities of their sodium salts: (2) the di-imide is hydrolysed similarly at 210° C. to the tetracarboxylic anhydride; the latter dissolves in solutions of alkalies from which solutions the tetracarboxylic acid is precipitated by acids; the calcium salt thereof, on heating, yields perylene: (3) tetrachlorperyene tetracarboxylic di-imide (obtained by chlorinating the di-imide) is similarly hydrolysed to the corresponding anhydride at 230-235° C.; the product dissolves in solutions of alkalies from which solutions the acid or the anhydride are precipitated by acidfying according as the solution is cold or hot. Perylene 3:4:9:10-tetracarboxylic acid yields vat-dyestuffs when condensed with amines.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

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BRITISH PATENT No. 121294.

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ROYAL SOCIETY—GOVERNMENT GRANT FOR SCIENTIFIC INVESTIGATIONS.

APPLICATIONS for the year 1925 must be received at the Offices of the Royal Society not later than January 1st next, and must be made on printed forms to be obtained from the Clerk to the Government Grant Committee, Royal Society, Burlington House, London, W.1.

Publisher's Announcements.

The following Books can be obtained from Rea & Inchbould, Merton House, Salisbury Square, London, E.C.4.:

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Various numbers, parts of Vols 117 and 118 (1918/19) are only on sale at 2s. 6d. each.

THE GENERAL INDEX to VOLS. 1 to 100 can still be purchased at £1 .(Carriage Extra)

All communications should be addressed to the Manager, CHEMICAL NEWS, Merton House, Salisbury Square, London, E.C.4.

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THE CHEMICAL NEWS,

VOL. CXXIX. No. 3370.

MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

TELEPHONES:

Administrative Central 6521
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A NEW AND RAPID METHOD FOR THE REMOVAL OF PHOSPHATES IN SYSTEMATIC QUALITATIVE ANALYSIS.

By L. J. CURTMAN, C. MARGULIES and W. PLECHNER.

(Contribution from the Laboratory of Qualitative Analysis, College of the City of New York.)

INTRODUCTION.

The fact that zirconium may be quantitatively precipitated as phosphate in the presence of large amounts of mineral acid (Bailey, *Chem. Soc. Trans.*, Vol. 49, pp. 481-485; Nicolardot and Reglade, *Compt. Rend.*, Vol. 168, p. 348) suggested the use of a zirconium solution as a precipitant for phosphate in systematic analysis. The method proposed is directly applicable to the filtrate from Group 2 after boiling out the H_2S. It can therefore be readily adapted to any scheme of systematic analysis. It possesses many advantages over the old iron phosphate method which has been shown by Gilmour (*Chem. News*, Vol. 113, pp. 1-13) to be faulty in many particulars. In showing the application of the new method we have chosen the widely used scheme described on page 95 of Baskerville and Curtman's "Qualitative Analysis."

PHOSPHATE SEPARATION.

Boil out the H_2S from the filtrate from Group 2 and test it for PO_4 (note 1). If PO_4 is found, test for the presence of Groups 3, 4 or Mg (note 1). If both PO_4 and Groups 3, 4 or Mg are shown to be present, proceed as follows:

Add 2 g. NH_4Cl (note 2) and 10 cc. $ZrOCl_2$ solution drop by drop, stirring vigorously (note 3). Add 0.2 g. asbestos. Render alkaline with NH_4OH (note 4) and boil for 2 minutes. Neutralize with dil. HCl, add 10 cc. 3N HCl in excess and boil for 3 minutes (note 5). Filter hot, by gentle suction if available. If filtrate is not perfectly clear, refilter on the same paper. Filtrate should be clear (note 6). Test the filtrate for the presence of PO_4 (note 1).

Proceed with Scheme III., p. 96 ("Qualitative Analysis," by Baskerville and Curtman). The excess Zr will come down in Group III. (note 4). Proceed as directed in the scheme to the point where the Group III. precipitate is separated by means of HCl (1:9) into a *residue* of NiS and CoS,

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CHEMICAL NEWS, MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

and a *filtrate* containing the chlorides of the remaining metals of this group. The examination of the residue remains substantially the same as that given in the Scheme (note 7). The treatment of the filtrate is somewhat modified as follows: Evaporate the filtrate to one cc. and then dilute it with 10 cc. of water. Render alkaline with NaOH and add 10 cc. 6N NaOH in excess. Under hood, with caution, add Na_2O_2 a little at a time until 2 gr. have been added. Boil with stirring for one minute, dilute to 50 cc. (by comparison with a vessel of the same size containing 50 cc. of water) and boil again for one minute. Allow to settle and filter preferably by suction. If the filtrate is not clear refilter.

Residue may be $MnO_2.xH_2O$, $Fe(OH)_3$ and $Zr(OH)_4$ (note 8). If it is white, reject. If coloured, test for Fe and Mn. The Zr does not interfere with the tests for these metals.

Filtrate. The test for Al must be confirmed due to the presence of Zr. If the precipitate is slight, it is a trace of Zr or Al and may be rejected. To confirm the presence of Al, wash the precipitate into a beaker, make acid with dil. HCl and add 10 cc. 3N HCl in excess. Add sufficient water to make the volume 50 cc.; add 2 g. NH_4Cl and heat to boiling; add 1 cc. N Na_2HPO_4, boil and reject the precipitate of $Zr(OH)PO_4$. Make the filtrate just alkaline with NH_4OH and the Al will be precipitate as $Al(OH)_3$ or $AlPO_4$. The usual tests for Cr and Zn are not interfered with by the presence of Zr.

NOTES.

1. *Test for* PO_4. To 5 cc. of the solution add 2 cc. of conc. HNO_3 and evaporate to dryness to remove HCl which interferes with the test for PO_4. Take up with 2 cc. water and 1 cc. conc. HNO_3, heating if necessary to effect solution. Add 3 cc. ammonium molybdate reagent and heat. A yellow precipitate shows the presence of PO_4. The amount of PO_4 may be estimated by the size of the precipitate obtained.

Test for Groups 3, 4 or Mg. Make 5 cc. of the solution alkaline with NH_4OH. A precipitate shows the presence of Mg or one or more of the metals of Groups 3 or 4. If no precipitate is obtained, it is needless to remove PO_4 and in that case pass on to Scheme V.

2. NH_4Cl is added to aid in the precipitation of $Zr(OH)PO_4$, and, later, the sulphides of Group 3.

3. The precipitate formed is $Zr(OH)PO_4$. Since Zr and PO_4 react with each other in the ratio of 90:96, it follows that 1 mg. of Zr will precipitate approximately 1 mg. of PO_4. The $ZrOCl_2$ solution used contains 50 mg. Zr per cc.; hence 10 cc. of the solution will precipitate 500 mg. PO_4. If more PO_4 is likely to be present, add correspondingly more Zr solution. An excess of Zr solution is not harmful since the greater part is removed in the next operation.

Sometimes a precipitate will not appear on adding the $ZrOCl_2$ even though PO_4 is present; when this happens, it is an indication either that the amount of PO_4 is small, or that the $ZrOCl_2$ was added too rapidly. However, a precipitate of $Zr(OH)PO_4$ will form later when the solution is made alkaline and boiled.

4. $Zr(OH)PO_4$ precipitates best in alkaline solution. The addition of asbestos aids in the precipitation of the PO_4. Rendering the solution alkaline also precipitates the excess of Zr as $Zr(OH)_4$. The latter, on boiling, becomes fairly insoluble in dilute acids; so that all of the PO_4 and most of the exsess Zr are removed in one operation.

The maximum amount of Zr remaining in solution under these conditions is 15 mg.; when, however, the amount of PO_4 present is large, very little or no Zr will pass through.

5. The solution is boiled with HCl to insure the complete solution of the hydroxides of the metals of Group 3 which were precipitated on the addition of NH_4OH.

6. Occasionally a cloudy filtrate is obtained due to finely-divided or colloidal $Zr(OH)PO_4$ passing through the filter. When this is the case, the test for PO_4 in the filtrate will be valueless because the colloidal $Zr(OH)PO_4$ contains sufficient PO_4 to give a decided test. However, if all the PO_4 except that causing the cloudiness is removed, subsequent tests for the metals of Groups 3, 4 or Mg will not be interfered with. The colloidal $Zr(OH)PO_4$ will be carried down completely in the Group 3 precipitate yielding on filtration a clear solution free from PO_4. Since the small amount of PO_4 which may be mechanically carried into Group 3 is completely combined with the Zr, the former will not cause any of the metals of Group 4 or Mg to precipitate in Group 3.

7. Usually the (1:9) HCl will dissolve all the 15 mg. Zr. However, a small amount

sometimes remains; therefore if the residue left after the HCl (1:9) treatment is white it is $Zr(OH)_4$ and should be rejected. If, on the other hand, the precipitate is colored, it may still contain Zr. Should the precipitate formed by adding an excess of NaOH to the aqua regia solution of the sulphides of Ni and Co be insoluble in an excess of acetic acid, filter it off and reject it, for it is $Zr(OH)_4$.

8. Under these conditions about 10 mg. Zr will precipitate with the Fe and Mn, while 5 mg. will remain in solution. The latter will come down with the Al. This of course is true provided 15 mg. Zr are carried into Group III. If, however, smaller amounts of Zr are present (see note 4) correspondingly smaller amounts will appear at this point.

Confirmatory Experiments.

A—*Precipitation of Phosphate with Zirconium Oxychloride.*—The following experiments were performed for the purpose of determining the best conditions for the precipitate of phosphate as zirconium hydroxy phosphate by means of zirconium oxychloride. Zirconium oxychloride was used, as this salt is stable in aqueous solutions. A solution of strength 50 mg. Zr per cc. was used throughout.

1. 500 mg. PO_4 as H_3PO_4 in a volume of 125 cc. were treated with 10 cc. 3N HCl and with 10 cc. $ZrOCl_2$ solution, and the mixture filtered. The filtrate gave a test or PO_4 showing that the precipitation was incomplete.

2. *Effect of Boiling.* The experiment was repeated except that the mixture was boiled after the addition of the $ZrOCl_2$. It was found impossible to obtain a clear filtrate.

3. *Effect of Addition of* NH_4Cl *and Asbestos. 500 mg.* PO_4 *in a volume of 125 cc.* were treated with 10 cc. 3N HCl, 2 g. NH_4Cl, 10 cc. of the $ZrOCl_2$ solution and 0.2 g. asbestos. The mixture was then boiled and filtered. The filtrate was cloudy; but the cloudiness was removed after repeated filtration through the same filter paper. The clear filtrate was then tested and a small amount of phosphate was found to be still unprecipitated.

4. *Effect of Slow Addition of* $ZrOCl_2.PO_4$. Experiment 3 was repeated except that the $ZrOCl_2$ was added drop by drop to the boiling solution. The filtrate obtained was slightly cloudy but became clear on a second filtration through the same filter paper. The clear filtrate gave a negative test for PO_4.

5. *Effect of Large Excess Zr.* When 50 mg. PO_4 were precipitated with 10 cc. $ZrOCl_2$ under conditions of method "4" the precipitation was incomplete. This probably was due to the presence of a large excess of Zr. Therefore, with method "4" the amount of Zr used must be adjusted so as not to have too great an excess.

6. *Effect of Addition of* NH_4OH *and Reacidification.* 500 mg. PO_4 as H_3PO_4 in a volume of 125 cc. were treated with 10 cc. 3N HCl, 2 g. NH_4Cl, 0.2 g. asbestos and 10 cc. $ZrOCl_2$ added drop by drop to the boiling solution and further boiled for two minutes; it was then made acid with HCl, 10 cc. 3N HCl added in excess, and the resulting mixture boiled for three minutes and then filtered. The filtrate although cloudy, became clear on refiltration. No phosphate was found in the filtrate.

7. *Addition of* $ZrOCl_2$ *to the Cold Solution.* Experiment "6" was repeated except that the $ZrOCl_2$ was added to the cold solution and then made alkaline without previous boiling. The mixture was then boiled and the treatment completed as described in Experiment 6. The filtrate was clear and gave a negative test for PO_4.

8. *Minimum Amount of* PO_4 *Precipitated.* Repeated Experiment 7 using only one milligram of PO_4. The phosphate was completely removed.

9. *Effect of Rapid Addition of* $ZrOCl_2$. Experiment 7 was repeated adding the $ZrOCl_2$ rapidly. No precipitate formed even after stirring, but on completion of the experiment, phosphate was completely removed, evidently having come down when the solution was made alkaline.

Conclusion. Method 7 is the best since it completely removes the phosphate, makes unnecessary the adjustment of the amount of $ZrOCl_2$ to be added and does not require that the $ZrOCl_2$ be added drop by drop.

(To be continued.)

RING CHAIN TAUTOMERISM, PART I. ERRATA.

The Chemical News 1924, CXXIX, 283.

Page 283. Read the bottom line of formula (2) as COOH.C.MeOH and Page 284, the bottom line of formula (5) as CHMeCO.

CRITICAL STUDIES ON METHODS OF ANALYSIS.

XIV.: CHLORINE.

By LEON A. CONGDON, W. B. CRABTREE, H. W. COLES, L. L. SMITH, and M. L. VEHALGO.

(Contribution from the Department of Chemistry, Syracuse University).

INTRODUCTION.

Since Northmere (1) demonstrated the elementary nature of chlorine in 1805-6 by the condensation of the gas, this element, while not found free in Nature because it reacts so readily with many other substances, particularly metal, has considerable significance. The abundance of chlorine as sodium chloride or common salt and the large number of other compounds of chlorine both inorganic and organic has resulted in many investigations for its exact estimation. Nevertheless, it is surprising how few principles have been brought forth for the determination of chlorine since Marggraff (1709-82) estimated silver gravimetrically as the chloride. Gay-Lussac (2) in 1832 estimated silver and chlorine accurately as Agcl volumetrically by the precipitation method. F. Mohr (3) in 1856 modified Gay-Lussac's method for silver and chlorine by using an indicator, advantage being taken of the fact that silver combines with chlorine in the presence of a chromate, Ag_2CrO_4 being decomposed as follows:—$Ag_2CrO_4 + 2\ NaCl = 2\ AgCl + Na_2CrO_4$, and when all the chlorine has gone into combination of AgCl, an excess of $AgNO_3$ with the indicator, K_2CrO_4, immediately forms the red Ag_2CrO_4, which shows the reaction of $AgNO_3$ with the chloride to be complete.

Further modifications of Gay-Lussac's principle were brought forth by Charpentier (4) in 1870 and independently by J. Volhard (5) in 1874, which modification is generally known as Volhard's Thiocyanate volumetric precipitation process with various indicators used such as ferric alum, ferric sulphate or nitrate, etc.

Some investigations have been reported in the literature giving procedures for the estimation of chlorine in the presence of other halogens. Some of the principles upon which these processes are based are as follows:—Vortman (8) used a method depending on the different behaviour of chlorine, bromine, and iodine in the presence of acetic acid, with manganese and lead peroxide. Lyte (9) gives a method for the determination of Cl, Br and I in the presence of one another by first precipitating the halgens together with $AgNO_3$, the precipitate collected, dried, and weighed. This precipitate is then dissolved in about 30 or 40 times its weight of water by the addition of the least quantity of KCN. A quantity of pure KBr is now added, which need not be above the weight of the precipitate. The cyanide is now decomposed by the addition of an excess of dilute H_2SO_4. The precipitate in which any Agcl has become by this means converted in AgBr, is now collected on a filter, dried, and weighed. It is once more dissolved by the least possible quantity of KCN, and the same quantity of water, and to this is now added one and a quarter times the original weight of the precipitate of KI. The cyanide is now again decomposed by dilute H_2SO_4 and the precipitate once more collected on a filter, dried and weighed. In this last precipitate all the silver is converted into iodide, excepting such as was iodide already. In the second experiment all became bromide, excepting such as was bromide or iodide already. From the weights obtained in the 1st, 2nd, and 3rd weighings, the chlorine, bromine, and iodine may be easily calculated.

Benine (10) finds a convenient method of estimating the chlorine ion in the presence of iodine ion by precipitating them as silver salts and treating the precipitate with a measured excess of standard potassium ferrocyanide solution. This reacts with the silver chloride, forming an insoluble silver potassium ferrocyanide, which is filtered off, and the excess of ferocyanide titrated with standard $KMnO_4$. Jannasch and Aschoff (11) have worked out a method for estimating chlorine, iodine, and bromine in a mixture. The chlorine is estimated in the presence of iodine and bromine by liberating the iodine with HNO_3, removing iodine with CS_2 or steam, and the bromine is oxidized with $KMnO_4$ and CH_3COOH and then removed with steam, after which the chlorine is precipitated in the regular way. The chlorine, in the presence of iodine in a solution, may be estimated by adding ammonium sulphate solution and alcohol and the iodine precipitated with thallous sulphate. After filtering off the thallous iodide, the chlorine is estimated in the solu-

tion by $AgNO_3$ in the regular way. White (12) estimates chlorine in the presence of bromine and iodine by removing the bromine as a precipitate with aluminium sulphate and $KMnO_4$. The iodine is distilled off by first adding ferric chloride, chromic acids, and H_2O_2. The chlorine is then estimated in the regular way with $AgNO_3$.

Bokk (13) has modified Baubigny's method for the determination of chlorine, bromine, and iodine in the presence of each other. The total halogens are precipitated with an excess of $AgNO_3$ and weighed as total halogens of the silver salts. The iodine is then oxidised to HIO_3 and the chlorine and bromine are liberated as free halogens by treating a second portion of the precipitated moist washed silver salts with $K_2Cr_2O_7$ in concentrated H_2SO_4 solution and digesting for half-an-hour, the chlorine and bromine being expelled by a stream of air. A concentrated solution of Na_2SO_3 is added to the diluted filtered solution in order to reduce the hydriodic acid, and the iodine is then estimated in the regular way as silver iodide. Finally, the filtrate containing the silver, formerly with the chlorine and bromine, is treated with KI in sufficient amount completely to precipitate the silver in AgI, and this is filtered, washed, and weighed. From the three weights, it is then easy to estimate the chlorine, bromine, and iodine in the sample.

Weiss (14) suggests the following for the separation and determination of chlorine, bromine, and iodine. He heated the substance to be examined in a current of air with ferric sulphate (moderately strong solution), receives the iodine in a strong solution of KI, and titratesi t with $Na_2S_2O_3$. The residue is cooled, mixed with $KMnO_4$, heated to 50° to 60°, and treated with a current of air. The bromine evolved is received in ammonia and determined by titration, or preferably gravimetrically as AgBr. The chlorine is then calculated from the difference.

A few methods have been developed for the determination of various forms of chlorine in a mixture of the same, such as hydrochloric, chloric, and perchloric acids by reduction methods with $Ca(OH)_2$ in a platinum dish, or by reduction with H_2SO_3, or by fusion with alkali carbonate, 1 to 3. This gives the total chlorine content by precipitation with $AgNO_3$ in the usual way, and the chloride can be estimated in a separate portion by the usual manner as Agcl. It is then easy by using appropriate factors to estimate the three forms of chlorine. Other reducing agents have been suggested and used, such as zinc dust in acetic acid solution, or SO_2 gas has been used. The principle being the fact that chlorine must be in the form of hydrochloric acid or chloride before it can be estimated as AgCl by means of HNO_3 and $AgNO_3$.

While the principle used in the estimation of chlorine when present in more than one form is almost always one of reduction in which the resultant chloride is estimated in the regular way and separate portions used for the chloride originally present, the principle underlying almost all existing methods for the separation of the halogens when present together is that of differential oxidation, and the so-called " oxidation potential " of all the oxidation agents recommended is, with one exception, higher than that of an acqueous solution of chlorine. It is therefore necessary, in order that good results can be obtained, to accurately interrupt the process when the whole of the bromine has been distilled over and to pay minute attention to the experimental conditions, especially the degree of acidity and concentration. Iodic acid constitutes the exception referred to above, and was proposed by the separation of bromine and chlorine by Bugarszky (36). Iodic acid has an " oxidation potential " which lies between that of chlorine and that of bromine and hence it is well suited for the separation of these two halogens. Andrews (32) has submitted this method to investigation and made certain improvements, and finds it well suited for the separation of these halogens. Further work by Jannasch (37) shows a method for the quantitative separation of iodine from chlorine and bromine, in which the mixture containing them is dissolved in a solution of H_2O_2 strongly oxidified with acetic acid, and the liberated iodine distilled over with steam and collected in an ammoniacal solution of hydrazine sulphate. He also deals with the separation of bromine and chlorine and shows that solutions acidified with H_2SO_4 and containing H_2O_2 the former halogen may be distilled over a current of CO_2, leaving the chloride undecomposed. These separations, more particularly that of iodine, appear to be very complete, and the methods seem to be realizable. He obtained good results for chlorine and iodine, while those for bromine were slightly low. Wager's (38) method of

separating silver halides when only the chloride and iodide are present is based on the fact that these may be separated quantitatively by treatment at 70°—80° with a solution containing 10 grams of ammonium sesquicarbonate and 20 cc. of 20% ammonia per litre, this dissolving the AgI only. Baubigny (39) has modified this method and shows also that an ammoniacal solution of AgCl or AgBr, when heated with iodic acid, only deposits AgI when a temperature of 200° is reached.

(To be continued.)

THEORY OF DETERMINATION OF ULTRA-RADIO FREQUENCES BY STANDING WAVES ON WIRES.

By August Hund.

Dept. of Commerce U.S.A.

Abstract.

This paper furnishes the theoretical background for the method of frequency standardization employing short standing waves on parallel wires. The three essential differences between the parallel-wire system employed by the Bureau of Standards for frequency standarization and the classical system are these: High-frequency voltages are impressed on the wires instead of being caused by discharges originating on the wires; the waves produced are continuous instead of being damped; an electron-tube generating set being substituted for the spark-gap circuit; a current-indicating instrument is used instead of a device for indicating voltage nodes.

The discussion shows that correct results can be obtained by the Bureau of Standard's method if the correction derived in the paper is employed in the calculation of the frequency. It is shown that the adjustment is based on a condition of resonance and, therefore, the settings are sharp, and it is practical to approach the theoretical accuracy in actual operation for frequency standardization.

The main part of the paper gives the practical deductions that may be drawn from the mathematical theory and also the method of calculating the correction to be used in calculating the frequency. The Appendix gives the complete mathematical theory of the action of standing waves on parallel wires with special consideration to the system as used at the Bureau of Standards.

In his introduction, Mr. Hund says that accurate knowledge of the frequency of the waves and the currents used in radio comnication is of great importance, and the Bureau of Standards has recently increased the accuracy of its standard of radio frequency. The standard has been established by methods which cover a wide range of frequencies and which give the desired accuracy. One of the methods is based on the use of very short waves, the length of which is directly measured on a system of parallel wires. The standard wave-meter may be compared with the frequencies of these short waves by means of the harmonics from a local generating set.

A similar procedure was used in the earliest days of radio. There are, however, three essential differences between the parallel-wire system employed by the Bureau of Standards and the classical two-wire system, namely: (*a*) the high-frequency voltages are impressed on the wires instead of being caused by discharges originating on the wires; (*b*) they are sustained instead of being damped; and (*c*) a current-indicating instrument is used instead of a device for measuring voltage.

GENERAL NOTES.

MINERAL PRODUCTION IN CANADA IN 1923.

The output of gold during 1923 totalled 1,243,341 fine ounces, valued at $25,702,139, a decrease of 1.5 per cent. below the level of the previous year. Ontario was the principal contributor, producing gold to the value of $20,293,622, while British Columbia's' output was valued at $4,137,261. The Yukon produced $1,243,-287. The production of silver in Canada showed a creditable increase, the output for the past year reaching 18,601,714 fine ounces, which was valued at $12,067,509. The 1922 production totalled 18,626,439 fine ounces, valued at $12,576,758. While the above figures would indicate a very small decrease it should be noted that the production reported for 1922 included 1,222,450 fine ounces which was added in adjustment to take account of the silver bullion on hand

at the end of 1921 that had not previously been included in the reports on the mineral production of Canada. The production by provinces follows: Ontario, $6,838,226; British Columbia, $3,965,899; Yukon Territory, $1,241,953; Quebec, $21,412; other provinces, $19. The production of the metals in the platinum group totalled 3,253 fine ounces, valued at $325,386

Canadian copper output doubled during 1923 reaching a total of 86,881,537 pounds, valued at $12,529,186. The 1922 production was 42,879,818 with a value of $5,738,177. There was a marked revival in the output of nickel from the ores of the Sudbury district. The production amounted to 62,453,843 pounds contained in nickel-copper matte and from silver cobalt ores, computed value of $18,332,077, as compared with 17,597,123 pounds from the same source in 1922. The total shipments of iron ore from Canadian mines amounted to 30,759 short tons, the net value of which was reported as $114,944, as against 17,971 tons shipped in 1922 with a value of $56,993. The output included 30,447 tons of beneficiated magnetic from Ontario. The production of lead rose nineteen per cent. in 1923, amounting to 111,234,466 pounds, valued at $7,985,522 as compared with 93,307,171 pounds in 1922 with a value of $5,817,702. The production of chromite totalled 3,558 tons valued at $52,650. Two hundred tons of manganese were shipped during 1923.

The total quantity of asbestos rock mined during the year amounted to 3,768,542 tons. The mill recovery of marketable asbestos was 236,658 tons, including by-products, the value was $7,522,506. The production of crude petroleum was 170,169 barrels valued at $522,018, as compared with 179,068 barrels in 1922, with a value of $611,176. The output of salt amounted to 206,985 tons, of which quantity 202,397 tons valued at $1,713,516 were marketed. The sales for 1923 showed an increase of approximately 21,000 tons over 1922. During 1923 the total production of arsenic amounted to 7,344,202 pounds with a value of $883,771, as against 5,152,000 pounds valued at $321,037 in 1922.

BRITISH CHEMICAL INDUSTRY.

A more cheerful tone has been apparent in the chemical markets during the last few weeks, says the British Industries Federation Journal.

Production would have been better but for the depressed condition of the superphosphate industry which, together with sulphate of ammonia, normally consumes half the total output. The sulphate of ammonia industry is in a very strong position and appears fully capable of meeting any competition which other nitrogenous fertilisers might furnish. An important feature disclosed by figures given is the very great increase in the production of high quality acid from brimstone. In pre-war times this raw material formed less than 1 per cent. of the acid produced has been made from it, with great satisfaction to all concerned.

The prices of the heavy soda products, bleaching powder and other typical heavy chemicals have remained practically unaltered for some months past, ammonia alkali being quoted at £6 15s. per ton, f.o.r., and solid caustic soda at £16 17s. 6d. to £19 7s. 6d. according to strength, with contracts at 20s. less per ton. Soda crystals remain at £5 5s. to £5 10s. per ton, on railway depôts or ports, and soda bicarbonate at £10 10s. per ton. The demand for bleaching powder has improved lately, and the price is still about £11 for spot delivery and £10 per ton for contracts. Crude sulphuric acid 140 Tw. is quoted at an average price of 65s. per ton, and the 168° Tw. arsenical quality at £5 10s. per ton, with the non-arsenical at £6 15s. per ton. Acetic acid has been a firmer market, the 80 per cent. pure quality advancing to £47 per ton, but acetates of lime and lead have had a weaker tendency, brown acetate of lime falling to £12 and the grey to £16 per ton. Sal ammoniac and oxides of lead have also been in better demand of late. The producers of copper sulphate have recently formed an Association among themselves, and the product itself has been considerably firmer, although the price is still in the neighbourhood of £25 per ton. Arsenic still tends to decline in value and is now only £42 per ton f.o.r. Potash products are unchanged in price, the bichromate remaining at 5½d. per lb., chlorate at 2⅝d., and permanganate and prussiate both at 7d. per lb. Organic acids, other than acetic, remain very dull, particularly oxalic at 4d., citric at 1s. 4d., and tartaric at 1s. per lb.

The tar products section has been very quiet, and in spite of the restricted output

due to the reduced number of coke ovens in operation and the smaller production of gas in the summer months, prices have fallen to a comparatively low level. Cresylic acid has been the steadiest feature, and pyridine, owing to the demand for methylating purposes, maintains its high price of about 19s. per gallon. There have been signs of a better demand for solvent naphtha and for creosote lately, but prices are no better than 1s. and 6d. per gallon respectively. Although the pitch market should now be getting busy, the average price has been about 40s. per ton.

RESTRICTION ON SALE OF DANGEROUS DRUGS.

The Home Office has issued the subjoined tables to show the effect of British trade in morphine and heroin of the restrictive measures imposed by the British Government under the Dangerous Drugs Act, 1920, in fulfilment of the International Opium Convention of 1912:—

Years 1910 to 1923.

Year.		Quantity of morphine and its salts. Manufactured	Exported	Quantity of heroin and its salts manufactured.
		ozs.	ozs.	ozs.
		1.	2.	3.
1910	...	486,975	—	10,272
1911	...	406,877	208,544	3,785
1912	...	425,048	276,560	3,034
1913	...	564,035	406,160	11,665
1914	...	735,628	504,016	12,249
1915	...	926,743	295,568	29,756
1916	...	1,033,162	225,616	26,761
1917	...	751,851	124,592	47,338
1918	...	294,703	136,832	34,669
1919	...	547,347	322,912	84,414
1920	...	643,965	322,464	76,145
1921	...	115,734	77,364	12,385
1922	...	131,028	131,658	31,673
1923	...	87,940	98,831	11,576

Notes.—(1) Col. 1.—The figures of manufacture are the net amounts of morphine manufactured for use as such, and do not include morphine manufactured for conversion into heroin, codeine, or other alkaloids.

(2) Col. 2.—The export figures for 1911 to 1920 are compiled from the Customs Returns and do not include exports by parcel post or exports of preparations containing the drugs. The figures for 1921-23 are compiled from the returns made to the Home Office and include both exports by parcel post and exports of preparations containing the drugs.

(3) Col. 2.—The export figures for 1914-17 do not include exports on Government account between August 4, 1914, and June 30, 1917.

(4) Col. 3.—*Particulars of exports of* heroin and its salts are not available before 1921.

WORLD'S PRODUCTION OF GOLD.

The estimated value of the gold produced in the world from 1860 to 1922, inclusive, was $14,324,716,600. In 1922 the estimated production of gold in the world decreased $10,802,600, after a decrease of about $6,740,500 in 1921, of $28,769,000 in 1920, of $15,136,000 in 1919, and of $38,500,000 in 1918. The production in the United States decreased $1,218,200 and Africa $21,585,700. The large decrease in the Rand mines in South Africa was due to labour troubles in the first three months of 1922. There were fair increases in Canada, Mexico, and some South American countries.

The prevailing tendency during recent years toward a declining world output of new gold caused by the high cost of labour and supplies, which made the operation of many gold mines unprofitable, has been modified to some extent by greater political and financial stability in some countries, which will tend to increased operations or the re-opening of old properties.

NEW PRINCIPAL OF BRISTOL TECHNICAL COLLEGE.

Professor Andrew Robertson has been appointed principal of Bristol Merchant Venturers Technical College, in succession of the late Dr. Wertheimer. The new principal received most of his training at Manchester University, where he took his degree of B.Sc. in 1908 and the Fairbairn Prize. He was appointed Demonstrator in Engineering there the same year.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE ROYAL SOCIETY.

Nov. 6. Papers read:

1. T. R. MERTON, F.R.S.—*On Ultra-violet Spectro-photometry.*

The preparation of a "neutral wedge" of platinum is described. It has been found that such wedges can be used for measurements of radiations as short as $\lambda = 2100A$. These "wedges" require to be calibrated, both as regards the thickness of the platinum as a function of the distance from the thin end of the wedge, and as regards the density gradient for a given change in the thickness of the platinum as a function of the wave-length. A method for performing the necessary calibrations is described. The density gradient is sensibly constant from $\lambda = 4000A$ to $\lambda = 2500A$.

2. W. L. BRAGG, F.R.S., and S. CHAPMAN, F.R.S.—*A Theoretical Calculation of the Rhombohedral Angle of Crystals of the Calcite Type.*

The crystals of calcite may be regarded as an assemblage of ions, which are held together by electrostatic attraction and kept apart by repulsive forces which only come into play when the ions approach closely. The structure of calcite found by X-ray analysis is built on a series of rhombohedral cells, whose edges meet at an angle of 101° 55′. Other carbonates and sodium nitrate have a very similar form. The rhomhohedral angle of about 102° which is present in all cases is not fixed by the symmetry, and there must therefore be some fundamental reason, common to all these structures, for its observed value.

The angle has been calculated theoretically by a consideration of the equilibrium of the calcite structure. It is assumed that the electrostatic forces correspond to those which would act between a charge of $+2e$ at the centre of the calcium atom, $-2e$ at the centre of the oxygen atom, and $+4e$ at the centre of the carbon atom. It is further assumed that the force of repulsion is directed from the electrostatic centre of each atom. A small deformation of any time should he possible without an alteration, to the first order of approximation, of the potential energy of the structure. In our calculation the crystal is giving a deformation which does not alter the distance between neighbouring atoms, so that the forces of repulsion do no virtual work. The electrostatic energy for each configuration is calculated, and a value for the rhombo-angle found which makes the energy a minimum. This is the condition for equilibrium.

The rhombohedral angle so calculated differs by 3° or 4° from the observed value. Reasons for this discrepancy are discussed. The alteration in rhombohedral angle, when one metal is substituted for another, is very exactly explained.

3. O. W. RICHARDSON, F.R.S., and T. TANAKA—(1) *The Striking and Breaking Potentials for Electron Discharges in Hydrogen.*

This paper describes an experimental investigation of discahrges from a thermionic electron-emitting cathode in hydrogen at pressures below 1 mm. There are three types of discharge, characterised by different luminosity distribution and by other features. It is shown that the striking and breaking potentials for the discharge which sets in at the lowest voltages have the following properties:—(1) They fall to a limit as the electron emission of the cathode increases; (2) these limiting values have a minimum for a pressure which depends on the electrode distance; (3) as the electrode distance is diminished the minimum values of the breaking potential approach a lower limit asymptotically, but the behaviour of the striking potential is more complex. It is shown that the limit of the breaking potential thus reached coincides with the strongest ionization potential of hydrogen. Spectroscopic evidence is adduced in favour of the view that the type of ionization which occurs at this ionizing potential is the splitting of an electron from the hydrogen molecule with the formation of ionized H_2. A considerable number of the lines in the secondary spectrum have been found to be selectively affected as regards intensity in the different types of discharge.

5. J. D. BERNAL—*The Structure of Graphite.* Communicated by Sir William Bragg, F.R.S.

The structure of graphite has been examined by the method of the rotating single crystal. Sufficient evidence has been found to establish the latice proposed by Hull, rather than that proposed by Debye and Scherrer. This is confirmed by measurements by the ionisation spectrometer and

from Laue photographs. The structure has also been completely determined. It is essentially that of Hull, but with all the carbon atoms lying in the cleavage plane, as in the Debye and Scherrer model.

6. P. L. Kapitza *a-Ray Tracks in a Strong Magnetic Field*. Communicated by Sir Ernest Rutherford, F.R.S.

Photographs by the Wilson cloud method of α-ray tracks have been taken in magnetic fields of 40,000 to 80,000 gauss, produced by a method recently described by the author. The tracks are curved, and measurements of the curvature at front, on the track, give values for the ratio of the average charge to the velocity of an α-particle at various points along its range. The differences in curvature between individual tracks are investigated and explained as due to the natural curvature of α-particle tracks. The velocity curve of an α-particle close to the end of the range is obtained by using Rutherford's recent data on the capture and loss of electrons by α-particles.

Papers Read in Title Only.

7. C. N. Hinshelwood and R. E. Burk—*The Homogeneous Thermal Decomposition of Nitrous Oxide*. Communicated by Prof. J. W. Nicholson, F.R.S.

The bimolecular nature of the thermal decomposition of nitrous oxide into its elements has been confirmed by a more conclusive method than that previously used by Hunter.

The reaction is shown to be homogeneous from 838° abs. to 1.125° abs. and uncatalysed by platinum or rhodium.

The observed rate of reaction can be interpreted in terms of simple thermal activation of the molecules by collision.

8. C. N. Hinshelwood—*The Kinetics of the Interaction of Nitrous Oxide and Hydrogen*. Communicated by Prof. J. W. Nicholson, F.R.S.

The rate of interaction of hydrogen and nitrous oxide has been investigated in the absence of cataysts and in the presence of platinum. The rate of reaction on a platinum wire was followed by measuring the change in the thermal conductivity of the gas mixture as the reaction proceeds.

The results show that hydrogen forms a film on the platinum which retards the reaction. Nitrous oxide reacts with hydrogen when it enters the gaps in this film. The latent heat of evaporation of the film of adsorbed hydrogen, inferred from the effect of temperature on the rate of reaction, is about 25,000 calories per gram molecule.

10. K. R. Ramanathan *The Structure of Molecules in Relation to their Optical Anisotropy. Part I.* Communicated by Prof. C. V. Raman, F.R.S.

ROYAL SOCIETY OF ARTS AND COMMERCE.

John Street, Adelphi, London.

Papers to be read before Christmas. Ordinary Meetings.

Wednesday evenings, at 8 o'clock (unless otherwise announced).

November 12.—Colonel R. E. Crompton, C.B., R.E., M.Inst.C.E., M.I.E.E., etc., *The Motor Car, its Birth, its Present, and its Future*. Alan A. Campbell Swinton, F.R.S., will preside.

Nov. 19. — Llewelyn B. Atkinson, M.I.E.E., Past-President of the Institution of Electrical Engineers, *The Scientific Principles of Artificial Incubation*. Edward Brown, F.L.S., President of the International Association of Poultry Instructors and Investigators, will preside.

Nov. 26.—C. F. Elwell, B.A., *Talking Motion Pictures*.

December 3.—Professor C. A. Carus Wilson, M.A., F.R.A.S., *The Teaching of Science in Secondary Schools*. Sir Robert Abbott Hadfield, Bt., D.Sc., F.R.S.

Dec. 10.—(5 p.m.). Norman Thomson, *Columbia as a Field for Development*.

Indian Section.

Friday afternoon, at 4.30 o'clock.

Dec. 5.—Lieut.-Colonel R. McCarrison, C.I.E., M.D., B.Ch., B.A.O. (R.U.I.), LL.D., D.Sc., F.R.C.P., Indian Medical Service, *Problems of Food, with Special Reference to India*. Professor Henry E. Armstrong, Ph.D., LL.D., D.Sc., F.R.S., will preside.

Cantor Lectures.

Monday evenings, at 8 o'clock.

Louis C. Martin, D.I.C., A.R.C.S., D.Sc., Lecturer in the Department of Optical Engineering and Applied Optics, Imperial College of Science and Technology, South

Kensington, *Modern Colour Problems*. Three Lectures. November 24, December 1 and 8.

Lecture I.—The relations of light and colour. The physical basis of colour vision. The production of artificial daylight. Early efforts and modern improvements. The application of artificial daylight for time saving in industry.

Lecture II.—The psycho-physical basis of colour measurement. Specification of colour in terms of three variables. Colour systems and charts. Definite problems in colour measurement and their importance in Commerce.

Lecture III.—Colours of material objects. Some colorimeters and their possible accuracy. Limited range colorimeters and Tephelometers. General lines of progress. Probable limitations of these methods.

V. E. PULLEN, Director, Radiological Research Department, Woolwich, *Radiological Research A History*. Three Lectures. January 19, 26, February 2.

Lecture I.—Natural Philosophy. The border line between science and philosophy. Early natural philosophy. Development of theory. Discovery of X-rays. Controversy as to their nature. Modern theory concerning X-rays. Relation to modern atomic theory.

Lecture II.—Early apparatus. Early X-ray generators. Early vacuum tubes. X-ray tubes. *Development of electrical generators. Development of X-ray tubes.* The X-ray spectrometer. Measuring apparatus. Lines of modern radiological research.

Lecture III.—Early applications of X-rays. Development of medical uses. Modern applications. Physiological dangers. Necessity for protection.

WALTER ROSENHAIN, B.A., B.C.E., D.Sc., F.R.S., Superintendent of the Department of Metallurgy and Metallurgical Chemistry at the National Physical Laboratory, *The Inner Structure of Alloys*. Three Lectures. February 16, 23, March 2.

THE INSTITUTION OF ELECTRICAL ENGINEERS.

Paper read on Nov. 6:

An Electric Harmonic Analyser, by J. D. COCKCROFT, R. T. COE, J. A. TYACKE, and MILES WALKER.

The paper deals with the experimental harmonic analysis of electromotive force and current wave-forms. A brief outline of existing methods is given and their limitations discussed. A modification of the dynamometer method, which allows a much higher degree of accuracy to be attained, and in which the properties of an oscillatory circuit are used to obtain a sinusoidal current wave of suitable frequency, is described. This current is passed through one coil of a dynamometer, whilst the wave to be analysed is passed through the other. The values of the coefficients in the Fourier series representing the wave-form being analysed are obtained from the readings of *the dynamometer and an ammeter.*

The final method advocated aims at analysing wave-forms up to at least the 23rd harmonic and correct to within 0.1 per cent. of the fundamental. The accuracy of the method must be established by comparison with a method more accurate than the commonly employed oscillograph method, the accuracy of which is considerably improved upon. Such a standard method, which involves the use of a synchronously driven commutator, is dealt with in detail in the first part of the paper and its own accuracy is established. Most of the principles involved are common to the two succeeding methods. A full discussion of the errors involved in the three methods is given, and the design of the necessary instruments is considered. For convenience, *most of the mathematics involved is given in appendixes, and only the results are* quoted in the paper itself.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

At the opening meeting for the 1924-25 Session of the above Institution, which was held at the House of the Royal Society of Arts, John Street, Adelphi, W.C.2, on the 7th October last, the following awards of Medals and Scholarships were announced:

The Boverton Redwood Medal has been presented to the Institution by Mr. Alexander Duckham to commemorate the late Sir Boverton Redwood, Founder and First President of the Institution, is awarded to the author of the paper of the greatest merit on any subject connected with Petroleum Technology, presented to the Institution during two consecutive sessions; preference being given to original work.

The award is not confined to members of

the Institution, and can be withheld if the Council consider that no paper of sufficiently outstanding merit has been presented.

It has been decided that the award should be made retrospective to 1919, the date of Sir Boverton Redwood's death, and so for the Sessions 1919-20 and 1920-21, it has been awarded to M. Paul de Chambrier, of Pechelbronn, for his paper on the "Working of Petroleum by means of 'Shafts' and 'Galleries,'" which was read before the Institution on the 15th February, 1921.

It is hope dthat if M. Paul de Chambrier can be present, the medal will be presented to him at the seventh annual dinner of the Institution, which is to be held at the Connaught Rooms, Great Queen Street, London, on the 17th March next.

As there was no paper of outstanding merit for the Sessions 1921-22 and 1922-23, no award has been made for those Sessions.

The Students' Medal and Prize, given by the Institution, is awarded to the Student Member of the Institution who presents the best paper on any subject connected with Petroleum Technology, in any one Session.

The Medal and Prize has been awarded to Lieutenant J. H. Blakiston, R.N.R. (late Student of the Oil Technology Course at Birmingham University), for his paper entitled "The Oilfields of Roumania."

This is the first award of this Medal and Prize.

The Institution's Scholarships are awarded annualy, one each to the Royal School of Mines, Imperial College of Science and Technology, London, and to Birmingham University, to a 3rd Year Student, taking the Petroleum Technology Course, who is also a Student Member of the Institution.

The award is made on the recommendation of his Professors, and is to assist him with his 4th year studies.

The award to the Student at the Royal School of Mines has been made to Mr. Ernest Clark, and the award to Birmingham University will be announced shortly.

SOCIETY OF GLASS TECHNOLOGY.

The first meeting of the Society of Glass Technology for the Session 1924-25 was held in Sheffield on October 15th, the President, Col. S. C. Halse, in the chair. An address entitled "The Present Position of the Glass Industry in North America," was given by Prof. W. E. S. Turner, D.Sc., who observed that in America the period of trade depression had not been continuous, as was the case in the United Kingdom. In the autumn of 1922, American Trade began to improve, and 1923 was a good yaar. In February, 1922, trade in general began to fall off, and a very dull period still persisted.

The cut-glass industry had almost entirely died out in America, but coloured glass was finding a place more and more. There was a distinct improvement in American taste for Glassware. At the Steuben Works of the Corning Glass Company some very fine artistic work was being manufactured.

Prof. Turner next referred to the gradual disappearance of pot furnaces in favour of tank furnaces. The latter was now being used even for the manufacture of green and blue signal lights, and for selenium ruby glass. Electric light bulbs, except in the case of very small or very large bulbs, were now practically all made by machines fed from tank furnaces, the glass being the soda-lime-magnesia type. The tubing required for the completion of the lamp was still of the glass variety.

Several noteworthy advances in the glass industry were the noted. During the past years there had been a very distinct development in the use of blowing machines or press and blow machines. In this connection reference was made to (1) the Westlake Machine for thin walled tumblers, (2) the Hartford-Empire Machine for electric light bulbs, and (3) the great development in the manufacture of light walled tumblers.

Dealing next with sheet glass, Prof Turner remarked that the Fourcault process had not as yet achieved any considerable success in America. The cylinder process was still in active operation. An epoch-making process was that developed at the Glass works of the Ford Motor Company. This process marked an absolute departure from the use of pot furnace, as the glass was melted in tanks, and there was continuous rolling between a pair of rollers, the sheet passing down a lehr about 440 feet long and subsquntly, in sheets, traversed long tables in a continuous belt, where the grinding and polishing was done.

With regard to bottle machine there was a tendeney to replace the Owens machine in favour of the feeder-type. There were no striking advances in feeding devices, the Hartford Empire Feeder being the most in favour, followed by the W. J. Miller. One novelty in operation was the use of a rotat-

ing plunger, especially when large ware was being made.

Prof. Turner then dealt with the problems of furnace sand furnace efficiency. This was one of the foremost problems discussed by glass manufacturers. The average life of a tank operated by machines was 11 to 13 months. A table was presented showing for a number of factories the valve of the rate 7 fuel consumed to glass melter. Several factories could show a ratio as low as 0.6. In conclusion, reference was made to the innovation of the use of heatless lehrs. A description was given of such lehrs.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

SEPTEMBER-OCTOBER EXAMINATIONS, 1924.

PASS LIST.

The following candidates have passed the Examination for the Associateship:—

In General Chemistry.—Allister, Charles Fulton, Heriot-Watt College, Edinburgh; Austin, Reginal George, University College, Southampton; Bell, John Lindsay, Heriot-Watt College, Edinburgh; Browne, Thomas Ethelred Wilby, B.Sc. (Wales), University College, Bangor; Cochrane, Colin Galbraith, B.Sc. (Lond.), Heriot-Watt College, Edinburgh; Firth, Herbert, Bradford Technical School, Liverpool; Hallas, Charles Arthur, B.Sc. (Lond.), Northern Polytechnic Institute, and King's College, London; Lander, Miss Catherine Meads, University College, Nottingham; McGill, Alexander, Heriot-Watt College, Edinburgh; Ransome, Gerard Lione, B.Sc. (Lond.), The University, Cambridge; Rumford, Frank, Battersea Polytechnic; White, Walter Arthur, Sir John Cass Technical Institute; Williams, Kenneth Alan, B.Sc. (Lond.), Chelsea Polytechnic Institute.

Under Regulations prior to March, 1920.

In Metallurgical Chemistry. Claudet, Richard Arthur Omerod, B.Sc. (Lond.), King's College, London, and Sir John Cass Technical Institute.

The following candidates have passed the Examination for the Fellowship:—

In Branch A: Inorganic Chemistry. Morris, Edgar Archibald, B.Sc. (Lond.).

Branch D: Agricultural Chamistry. — Pyne, Gerald Thomas, A.R.C.Sc.I., B.Sc. (Lond.).

In Branch E: The Chemistry, including Microscopy, of Food and Drugs, and of Water. — Bagnall, Herbert Henry, B.Sc. (Birm.).

In Branch: Chemical Engineering. — Sensicle, Laurence Henry, B.Sc. (Lond.).

By Order of the Council,
RICHARD B. PILCHER,
Registrar and Secretary.

17th October, 1924.

THE OPTICAL SOCIETY.

The next meeting of The Optical Society will be held at The Imperial College of Science and Technology, Imperial Institute Road, South Kensington, at 7.30 p.m, on Thursday, 13th November, 1924,

The following papers will be presented and discussed:—

The back vertex power of a combination of lenses, by T. SMITH, M.A., F.INST. P.

The theory of neutralisation, by T. SMITH, M.A., F.INST. P.

A new type of nephelometer, by R. KINGSLAKE, A.R.C.S., B.Sc.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

The meeting of the Society was held on Wednesday, November 5th, at the Chemical Society's Rooms, Burlington House, Piccadilly, W. The following papers were read:

On certain new Methods for the Estimation of Arsenic and its Occurrence in Fish and Urine, by H. E. COX, PhD., F.I.C.

The Estimation of Cadmium in Brass, by A. A. ETHERIDGE, M.B.E., B.Sc., F.I.C.

The "Hoyberg" Method of Milk and Cream Testing, by N. C. WRIGHT, B.A., and J. GOLDING, D.S.O., F.I.C.

An Apparatus for the Catalytic Dehydrogeneration of Alcohols, by S. G. WILLIMOTT, Ph.D., B.Sc.

HABITS OF INSECTS.

ROYAL INSTITUTION: "Concerning the Habits of Insects" is the subject of the Ninety-ninth Course of Christmas Lectures to be delivered at the Royal Institution this year by Mr. F. Balfour Browne, Lecturer in Entomology at Cambridge. The first lecture is on Dec. 27 on Insect Collecting and what it leads to, followed by the Habits of Bees and Wasps (Dec. 30), Habits of Caterpillars (Jan. 1), Habits of the Dragonfly (Jan. 3), Habits of the Water-Beetle (Jan. 6), and the Habits of Insects and the Work of Man (Jan. 8).

NOTICES OF BOOKS.

Aniline and its Derivatives, by P. H. GROGGINS, B.Sc. Pp. vi. + 256. London: Chapman & Hall, Ltd., 11, Henrietta Street, W.C.2. 1924. 18/- net.

This American treatise on aniline and its derivatives has evidently been written for the manufacturer and the works chemist. It contains much useful technical information that is not given in the ordinary text books in dyestuffs. Not only are the actual processes described but the actual manufacturing details are included.

Organic chemists will be astonished at first when they discover that the author describes the preparation of nitrobenzene *after giving an account of its reduction to* aniline. Further reflection will show, however, that there is nothing exceptional in this since the book is not intended as a systematic textbook but as a practical guide, to be consulted in the works laboratory.

The reduction reactions, which have long been the source of much speculation, are considered, together with thermal factors and rectification processes.

Another long chapter is devoted to some of the derivatives and dyes obtained from aniline. A list of those used in the rubber industry is given on p. 225, and lists of aniline dyes are also given. Although readily converted into such, *para*-phenylene diamine is not a dyestuff itself (p. 197).

The introduction (dealing with the importance of the discovery of aniline dyes) to this eminently practical book, has apparently been abstracted from the Hoffman Memorial Lecture delivered in 1896.

Memoirs and Proceeds of the Manchester Literary and Philosophical Society 1923-24. Price 12/-. 36, George Street, Manchester.

Among the contents, papers on Coal-dust Explosion, Presidential address by H. B. Dixon, C.B.T., M.A., etc.; Surface Tension, Surface Energy, and Surface Layer, by A. M. Williams, M.A., D.Sc.; Thermo Dynamics in Physiology, by A. V. Hill, F.R.S.; The Psycho-Galvanic Phenomenon, by R. H. Thouless, M.A.; Medideval Metallurgy, by M. L. Becker, B.Me.; On Some Derivations from the Normal Morphology, by W. H. Lang, F.R.S.; Physical Research in the Cotton Industry, by A. E. Onley, M.A.; Some Problems Relating to Antartic Sea Ice, by R. W. James, M.A.; Tri-hybrid Primula, by Professor F. E. Weiss, D.Sc.; and the Literary and Philosophical Society 1781-1851, by Francis Nicholson, F.R.S.

A History of Bleaching, by S. H. HIGGINS, M.Sc. Pp. viii. + 176. Longmans, Green & Co., 39, Paternoster Row, London, E.C.4. 1924. 15/- net.

This interesting volume gives a description of bleaching in the earliest times, also of the development in the middle ages, of the effect of chemical inventions in the eighteenth century which made bleaching a branch of Chemical Industry, the development during the past hundred years.

Text-Books of Physical Chemistry. Edited by SIR WILLIAM RAMSAY, K.C.B., etc., and F. G. DONNAN, M.A., etc. Pp. x. + 408. London: Longmans, Green & Co., 39, Paternoster Row, E.C.4. 1924. 15/- net.

The Chemistry of Enzyme Actions, by GEORGE K. FALK, Harriman Research Laboratory, New York. Pp. 250. U.S.A. The Chemical Catalog Company, East 24th Street, New York. 1924.

Practical Organic Chemistry, by JULIUS B. COHEN, B.Sc., F.R.S., etc. Pp. xv. + 520. London: MacMillan & Co., Ltd., St. Martin's Street. 1924. 6/6.

The Constituents of Coal Tar, by PERCY EDWIN SPIELMANN. Edited by SIR EDWARD THORP, C.B., F.R.S. Pp. xii. + 220. London: Longmans, Green & Co., 39, Paternoster Row, E.C. 1924. 12/6.

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. V. B, Al, Ca, In, Tl, Sc, Ce, and Rare Earth Metals, C. (Part I.), by J. W. MELLAR, D.Sc. Pp. x. + 1004. London: Longmans, Green & Co., 39, Paternoster Row, London, E.C.4. 1924. 63/- net.

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co.. Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patest Applications.

24833—Carbide & Carbon Chemicals Corporation.—Processes of rectifying hydrocarbon mixtures. Oct. 18.

24493—Coke & Gas Ovens, Ltd.—Neutralizing free acid in sulphate of ammonia. Oct. 15.

2 4171—Evans, A. J.—Recovery of ferrous sulphate from waste pickle. Oct. 13.

25169—Breidig, G.—Production of hydrocyanic acid. Oct. 22.

25264—Harper, W. A. — Production of ammonia. Oct. 23.

Specifications Published This Week.

201540—Soc. of Chemical Industry in Basle. Manufacture of sulphurised dyestuffs and intermediate products therefor.

222587—Bone, W. A., and Finch, G. I.—Process of recovering ammonia from gases or vapours.

211096—Christenson, C. L.—Method for producing ammonium chloride from ammoniacal hot distillation or generator gases.

24755—Kaiser, K.—Manufacture of formalhyde. Oct. 17.

202985—Noll, Dr. F.—Process of manufacturing durable compounds containing active oxygen.

222718—Ewan, Dr. T.—Manufacture of alkali metal amides.

223015—Cocksedge, H. E.—Manufacture of sodium carbonate.

206512—Pollak, F.—Manufacture of condensation products from formaldehyde and urea, thio-urea, or their derivatives.

223082—Deguide, C. — Process for the manufacture of barium cyanide.

209757—Compagnie Generale Des Produits Chimiques De Louvres.— Manufacture of zinc sulphide.

215000—Ledoga Soc. Anon. & Maimeri, C. —Process for the preparation of diethyl-sulphate from ethylene.

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ROYAL SOCIETY—GOVERNMENT GRANT FOR SCIENTIFIC INVESTIGATIONS.

APPLICATIONS for the year 1925 must be received at the Offices of the Royal Society not later than January 1st next, and must be made on printed forms to be obtained from the Clerk to the Government Grant Committee, Royal Society, Burlington House, London, W.1.

INSTITUTE of CHEMISTRY of GREAT BRITAIN AND IRELAND.

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Incorporated by Royal Charter, 1855.

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THE GENERAL INDEX to VOLS. 1 to 100 can still be purchased at £1 (Carriage Extra).

All communications should be addressed to the Manager, CHEMICAL NEWS Merton House, Salisbury Square, London, E.C.4.

THE CHEMICAL NEWS,

VOL. CXXIX. No. 3371.

MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

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A NEW AND RAPID METHOD FOR THE REMOVAL OF PHOSPHATES IN SYSTEMATIC QUALITATIVE ANALYSIS.

By L. J. CURTMAN, C. MARGULIES and W. PLECHNER.

(Contribution from the Laboratory of Qualitative Analysis, College of the City of New York.)

(Continued from Page 301).

B—*Removal of Excess Zirconium.*

1. 15 mg. Zr as $ZrOCl_2$ in 125 cc. solution were treated with 2 g. NH_4Cl, the solution rendered alkaline with NH_4OH and boiled for 2 minutes. After acidifying with HCl, 10 cc. 3N HCl were added in excess and the mixture boiled for three minutes. A clear solution resulted, showing that 15 mg. Zr as $Zr(OH)_4$ dissolve under these conditions. The Zr in solution was then reprecipitated with NH_4OH.

2. Repeated "1" using 20 mg. Zr. A residue of $Zr(OH)_4$ was left after acidification and boiling. The filtrate was made alkaline with NH_4OH and a precipitate of the same size as that of "1" was formed.

3. Repeated "2" using 500 mg. Zr. The final precipitate of $Zr(OH)_4$ was of the same size as that of "1."

4. *Effect of Presence of* PO_4. 200 mg. PO_4 were removed with 10 cc. $ZrOCl_2$ according to procedure A—7. When the resulting filtrate was made alkaline with NH_4OH only a slight turbidity formed, showing that practically all the excess Zr was removed.

Conclusion. The maximum amount of Zr remaining in solution is 15 mg.; where, however, the amount of PO_4 present is large, little or no Zr goes into solution.

5. *Solution of* $Zr(OH)_4$ *in* (1:9) HCl.—15 mg. Zr as $ZrOCl_2$ in a volume of 125 cc. were precipitated with NH_4OH and the mixture boiled. The precipitate was then filtered off and washed. The residue was then treated with 60 cc. HCl (1:9). All of the $Zr(OH)_4$ dissolved.

6. Repeated "5" without washing the precipitate (so as not to remove the excess of NH_4OH) and using only 10 cc. HCl (1:9). A residue of $Zr(OH)_4$ was left.

Conclusion.—If insufficient HCl is used some of the $Zr(OH)_4$ may not dissolve but will remain with the Ni and Co sulphides. In systematic analysis the amount of HCl is reduced in neutralizing the ammonia adhering to the precipitate and in dissolving the hydroxides and soluble sulphides of the metals of Group 3.

7. *Appearance of Excess Zr in Ni-Co Separation.*—15 mg. Zr. as $Zr(OH)_4$ were treated with 4 cc. dil. aqua regia (1:1). Complete solution took place. A solution was then made alkaline with NaOH and a large excess of acetic acid (6N) added. A residue of $Zr(OH)_4$ was left. This was filtered off and the filtrate made alkaline with NH_4OH. A slight precipitate of $Zr(OH)_4$ formed. Therefore, a large excess of $HC_2H_3O_2$ may dissolve a small amount of $Zr(OH)_4$.

8. *Appearance of Excess Zr in Removal of Fe and Mn.*—50 mg. Zr as $ZrOCl_2$ in a volume of 11 cc. were made alkaline with 6N NaOH and 10 cc. added in excess. Then 2 g. Na_2O_2 were added, the mixture boiled for one minute, water added to make the volume 50 cc. and the mixture again boiled for one minute. A residue of $Zr(OH)_4$ was left and filtered off. The filtrate was acidified and then made alkaline with NH_4OH. A precipitate of $Zr(OH)_4$ formed, equal in size to that given by 5 mg. Zr.

9. Repeated "8" using only 10 mg. Zr. A residue was still left and the amount dissolved gave a precipitate of $Zr(OH)_4$ equal in size to that given by 5 mg. Zr.

10. Repeated "8" using 5 mg. Zr. In this case no residue was obtained.

SPECIAL NOTICE.

All MSS., Books for Review, Business Letters and Communications of every description should be sent to the offices as under, and not to any other address.

CHEMICAL NEWS, MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

Conclusion.—Therefore, under conditions for the precipitation of Fe and Mn about 5 mg. Zr remain in solution.

11. *Separation of Zr from Al.*—10 mg. $Zr(OH)_4$ were acidified with HCl. treated with 5 cc. 3N HCl in excess and boiled. The $Zr(OH)_4$ completely dissolved. To the solution were added 2 g. NH_4Cl and 1 cc. Na_2HPO_4 and the mixture boiled. The precipitate of $Zr(OH)PO_4$ was filtered off and the filtrate made alkaline with NH_4OH. No precipitate formed, showing that the Zr was completely removed by the PO_4. This method of separating Zr from Al is given in the procedure. The amount of Zr used was greater than that which would come down with Al in the regular course of the procedure, in order to make the results "safe."

C.—*Interference of Zr with the Detection of the Medals of Group 3.*—

1. *With Ni.*—0.5 mg. Ni as $Ni(NO_3)_2$ in 10 cc. solution were treated with 10 mg. Zr as $ZrOCl_2$ and the solution made alkaline with NH_4OH. On adding a few drops of dimethylglyoxime a red precipitate formed.

2. *With Co.*—0.5 mg. $Co(NO_3)_2$ in a volume of 10 cc. were treated with 10 mg. Zr as $ZrOCl_2$ solution and the mixed solution acidified with $HC_2H_3O_2$. Upon the addition of KNO_2 solution and heating, a yellow precipitate formed.

3. *With Co Bead.*—A mixture of 0.5 mg. Zr as $Zr(OH)_4$ was tested with a borax bead in the usual manner. A blue bead was obtained.

4. *With Mn.*—A mixture of 1 mg. Mn as $MnO_2.xH_2O$ and 20 mg. Zr as $Zr(OH)_4$ was tested with a sodium carbonate bead and $KClO_3$ in the usual manner. A green mass was obtained.

5. *With Fe.*—1 mg. Fe as $FeCl_3$ in a volume of 10 cc. was treated with 20 mg. Zr as $ZrOCl_2$ and the solution acidified with dilute HCl. Upon the addition of $K_4Fe(CN)_6$ a deep blue precipitate formed.

6. *With Al.*—10 mg. Zr as $ZrOCl_2$ and 1 mg. Al as $AlCl_3$ in a volume of 25 cc. were made alkaline with NH_4OH; boiled and filtered. The residue was acidified with Hcl and 10 cc. 3N HCl added in excess; the volume was then made up to 50 cc. and the mixture boiled. The precipitate dissolved completely. The solution was treated with 2 g. NH_4Cl and 1 cc. N Na_2HPO_4, the mixture boiled and the precipitate of $Zr(OH)PO_4$ filtered off. On making the filtrate alkaline with NH_4OH a precipitate of $Al(OH)_3$ of $Al(OH)_3$ or $AlPO_4$ formed.

7. Repeated "6" using 50 mg. Zr and no Al. The test for Al was negative.

8. Repeated "6" using 5 mg. Al and no Zr. No precipitate of $Zr(OH)PO_4$ formed, but the test for Al was positive.

9. Repeated "6" using 50 mg. Zr and 5 mg. Al. The test for Al was positive.

Test Analyses.—To test out the method, the following analyses were made:—

No.	Ni	Co	Fe	Mn	Al	Cr	Zn	Ba	Sr	Ca	Mg	PO_4
1	0	0	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	0	0	500
3	0	0	0	0	0	0	0	0	0	0	0	200
4	0	0	0	0	0	0	0	0	0	0	0	25
5	0	0	0	0	0	0	0	0	0	0	0	10
6	0	0	0	0	0	0	0	0	0	0	0	1
7	0	0	0	0	0	0	0	0	0	0	0	500
8	0	0	0	0	0	0	0	0	0	1	1	200
9	0	0	0	0	50	0	50	0	0	0	0	200
10	0	0	0	0	5	0	1	0	0	0	5	200
11	1	1	1	1	5	1	1	0	0	1	1	200
12	50	0	50	0	50	0	50	0	0	15	10	200
13	0	0	0	0	0	0	0	1	1	1	1	200
14	0	0	0	0	0	0	0	1	1	1	1	200

Comments.—The phosphate was completely removed in one operation in all these analyses. Positive tests were obtained for all the metals present while negative results were obtained for all metals absent.

In analyses "7" and "14" sulphuric acid and alcohol were present as these reagents are used for the precipitation of Group 4 before Group 2 in the method of Curtman and Frankel (*Jour. Amer. Chem. Soc.* (1914) p. 1093).

In analysis 11 the Zn was detected by the use of $Hg(SCN)_2$ reagent (prepared according to Dennis).

The test analyses show that the precipitate consisting of $Zr(OH)PO_4$ and $Zr(OH)_4$ does not "drag down" any Ca, Mg or any of the metals of Group 3 since a positive test for as little as one milligram of each of these metals was obtained after removing in each case 200 mg. PO_4.

SUMMARY.

1. A new and rapid method is proposed for the removal of phosphate in systematic qualitative analysis by the addition of $ZrOCl_2$ solution to the acid filtrate from Group 2.
2. Provision is made for the simultaneous removal of excess precipitant along with the phosphate precipitate.
3. Under the conditions which prevail in the precipitation of the phosphate and the removal of the excess of zirconium, a maximum of 15 mg. Zr passes into the Group 3 precipitate. Of this amount, 10 mg. precipitate with the Fe and Mn and 5 mg. come down with the Al. The present of Zr does not interfere with the tests for Fe and Mn. Since, however, the detection of Al is interfered with by the presence of Zr, provision has been made for the separation of these metals.
4. Numerous confirmatory experiments and test-analyses show the method to be trustworthy.

New York City, N.Y.

CRITICAL STUDIES ON METHODS OF ANALYSIS.

XIV.: CHLORINE.

By LEON A. CONGDON, W. B. CRABTREE, H. W. COLES, L. L. SMITH, and M. L. VEHALGO.

(Contribution from the Department of Chemistry, Syracuse University).

(Continued from Page 304).

The method of estimating iodide in the presence of bromide or chloride by oxidation with $KMnO_4$, extraction of the iodine with CCl_4 and titration with $Na_2S_2O_3$ was originally proposed by Sammet (40). Bray and Mackay (41) have shown this method gives results accurate to within 0.1%.

Some investigations have been carried out for the determination of chlorine in organic compounds where it is necessary to unlink the chlorine bond from the organic compound in order to precipitate the chlorine as chloride by the usual process. One of the oldest methods along this principle is that of Carius (15), where the substance is placed under pressure in a bomb glass tube with $AgNO_3$ and fuming HNO_3 and heated, and, after cooling, the bomb is opened and the chloride estimated in the usual manner. Various other methods are described in the literature for the decomposition of the organic substance where a bomb is not used. Piria and Schiff decomposed the organic substance by mixing with quick lime and Na_2CO_3 in a small platinum crucible which is inverted in a larger one, the space between the two being filled in with the mixture of Na_2CO_3 and lime. The crucibles are heated over the blast, contents cooled, and dissolved in HNO_3, and the halogen being determined in the regular way. Davies (16) describes three such methods, namely, fusion with Na_2CO_3 in a platinum crucible, fusion with NaOH in a nickel crucible, and ignition of an evaporated solution of calcium acetate with the organic substance. Results were said to be satisfactory in the Na_2CO_3 and NaCN methods, but low in the calcium acetate methods. Pringsheim (17) used Na_2O_2 for the decomposing agent, and after reducing bromic and iodic acids, if present, with sulphurous acid, the chlorine is estimated in ordinary way as AgCl. Stepanow (42) found that most organic halogen compounds, including many of the more stable aromatic types, are readily decomposed by metallic medium in absolute alcohol, the halogen then being estimated in the usual manner.

Among colorimetric methods for the estimation of small quantities of chlorine may be mentioned Ellms and Hauser's (18) principle based upon the intensity of the green coloration produced by orthotolidine.

Liebig (19) used the principle of adding standard NaCl solution to the substance containing the chloride in solution, and then dropped standard mercuric nitrate solution to the appearance of turbidity, the chlorine in the solution estimated by making allowance for the standard NaCl solution used. Linessier and Lignon (20) made a gravimetric method by precipitation of the chloride with mercurous nitrate, filtering, washing the precipitate by decantation, drying, and weighing as HgCl.

Several indirect methods for the estimation of the halogens may be mentioned. Gooch and Perkins (43) made the sugges-

tion to estimate free halogens by shaking solutions containing them with a known weight of electrolytically deposited silver in an atmosphere of hydrogen and determining the increase in weight. Lasala (44) states that the halogens may be electrolytically estimated by an indirect method in which the halogen is precipitated as a silver salt, which is disolved in alkaline KCN solution, and the latter electrolyzed with a nickel-plated copper electrode and a rotating iron anode.

Investigations have been published for the procedure of determining chloride in blood, milk, wine, rubber, and ammoniacal liquors, etc. The only original thing about procedures being the method of attack for breaking up the substance by fusion with alkalines or decomposition of the substance by means of H_2O_2, etc. The end reaction in all cases being the estimation of the chloride by the usual gravimetric or volumetric process.

Picani (21) estimated small amounts of chlorine by a standard solutien of $AgNO_2$ and starch iodide. He acidified the chlorine solution with HNO_3, added an excess of the standard $AgNO_3$ solution, warmed, filtered, and determined the excess of Ag in the filtrate with starch iodide solution. From this he calculated the amount of silver combined with the chlorine.

Toressian (22) studied the iodometric estimation of chlorine in chlorides, and Kolthoff (23) worked on the iodometric determination of chloric acid.

For very small traces of chlorine, mixed with $(NH_4)_2SO_4$ and CuO, then heated in contacrt with hydrogen gas and examined the spectra.

In the present investigation three general methods, namely, Gay Lussac's gravimetric method as AgCl, Mohr's volumetric $AgNO_4$ precipitation method with K_2CrO_4 as indicator, have been studied with two salts of known purity, NH_4Cl and KCl. In addition in these methods, Linessier's and Lignen's gravimetric method as HgCl was tried on a sample of KCl of known purity.

Principles and Difficulties of the Methods Used.

Guy Lussac's gravimetric silver chloride method depends upon the fact that AgCl is only soluble to the extent of 0.000152 part per 100 parts of water at 20° and 0.0022 part per 100 parts of water at 100°. To the HNO_3 solution of the soluble chloride is added the silver nitrate solution as precipitant in slight excess. stirring during the addition of the reagent. The mixture is then heated and allowed to settle for half-an-hour in the dark. It is then filtered through a weighed Gooch crucible, washing the precipitate by decantation several times with cold water, slightly acid with HNO_3. It is finally transferred to the Gooch crucible and washed free of $AgNO_3$ with cold distilled water. The Gooch is dried for 15 minutes at 105° and then at about 130° to constant weight and weighed as AgCl, from which the chlorine is calculated. This procedure was used with the NH_4Cl sample. In the case of the KCl sample, the procedure was similar except that after drying at 105°, a drop of HCl and two drops of HNO_3 were added for the purpose of restoring the chlorine to any chloride that might have been reduced by light. The precipitate was then heated nearly to the fusion point, cooled and weighed as AgCl.

The only difficulty which might be encountered in the above method would be the very slight solubility of the AgCl in washing. Linde (25) has determined the error due to washing the AgCl with water. Constant stirring or agitation when the precipitant is gradually added reduces as much as possible the adsorption of salts by the precipitate and hastens coagulation of the AgCl. A test of the precipitate as to whether it is pure AgCl may be tried by dissolving in NH_4OH, and if no residue is left, it is free from silica, etc. If any difficulty is is experienced with the coagulation of the AgCl precipitate, Alifeld (26) has suggested the addition of 5 cc. of ether to the chloride solution before precipitation, and claims that this hastens the coagulation. Whittel (27) recommends a drop of chloroform to coagulate the AgCl. If the AgCl becomes violet or finally brown or black, the light has effected it and there may be a loss due probably to the formation of subchlorides according to Mulder (28).

Mohr's volumetric $AgNO_3$ precipitation method with K_2CrO_4 as indicator is a modification of Gay Lussac's original volumetric method, the modification being the use of an indicator added to the solution instead of depending on cessation of the precipitate of AgCl formed by a standard $AgNO_3$ solution and gauged by an experienced eye. Here is an application of the solubility product in the volumetric analysis. The re-

actions involved in this process may be expressed as follows:—

$AgNO_3 + KCl = AgCl + KNO_3$.

when the reaction is complete, any further addition of $AgNO_3$ reacts with the K_2CrO_4:

$2\ AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2\ KNO_3$.
(Red tint)

If acids are present, the chromate may form a dichromate which interferes with the recognition of the endpoint and dissolves appeciable quantities of the silver chromate. If the solution be alkaline, owing to the presence of a slight excess of carbonate if added, a little silver carbonate will be precipitated with the chromate, and hence neutralization shonld be effected with acetic acids. From the above, Mohr's process must be done in neutral solution.

Biscare (29) finds a defect in the volumetric determination of chloride by Mohr's process and makes note that if nitrates, especially those of the alkalies and earths, are simultaneously present, the precipitation of the red silver chromate often takes place too late, whether because such nitrates form double salts with $AgNO_3$ which are not precipitated by K_2CrO_4, so that a decided excess of Ag becomes necessary, or that the silver chromate already formed is slightly soluble in these waters. This observation is of especial importance in determinations of chlorine in organic bodies which have heen ignited witb lime and then dissolved in HNO_3. Besides the nitrates, other salts seem to interfere in a similar manner in Mohr's process. In this study where NH_4Cl was used as sample, high results were obtained by Mohr's volumetric process; but in the case of KCl as the sample analyzed, fairly good results were obtained by this process.

Charpentier's, or, as it is better known, Volhard's thiocyanate - precipitation volumetric process, is based on the fact that when solutions of silver and an alkali thiocyanate are mied in the presence of a ferric salt, the thiocyanate has a selective action towards silver, combining with this to form silver thiocyanate, any excess over that required by the silver reacting with the ferric salt to form the reddish brown ferric thiocyanate which shows the end of the reaction. In other words, this method is an indirect one in which the excess of silver used is determined in accordance with the following quotations:—

$AgNO_3 + KSCN = AgSCN + KNO_3$;
$3\ KSCN + Fe(NO_3)_3 = Fe(SCNy)_3 + 3\ KNO_3$.

The ferric thiocyanate differs from the great majority of salts in that it is but very little dissociated in acqueous solutions, and tbe characteristic color appears to be occasioned by the formation of the un-ionized ferric salt.

Soon after Charpentier's and also Volhard's papers, Brugelmann (30) in trying out the process found that the endpoint of the indicator was indistinct, explaining it, however, on the assumption that it was the free HNO_3 present that was destroying the color by oxidizing the sulphocyanate. This was in error, and the correct reason for the indistinct endpoint was first brought forth by Drechsel (31) who found that sulphocyanate of iron is decomposed by the AgCl first precipitate according to the following equation:—$Fe(SCN)_3 + 3\ AgCl = FeCl_3 + 3\ AgSCN$. He therefore recommends filtering off the AgCl before titrating with sulphocyanate. More recently Rosanoff and Nill (6) co-operate Drechsel's work and show that this filtering off the AgCl is a necessary modification of the thiocyanate process for chlorides. They find, however, that in case of bromides and iodides by this same proces the interference is negligible. Andrews (32) found that the presence of sulphate intereres with the thiocyanate process for chlorine, hecause appreciable quantities of silver sulphate are precipitated with the chloride and thiocyanate. Besides those mentioned that have studied the thiocyanate process for chlorine are the following:—Keninck (33), Knuefer (34), and Sanser (35). Their results show that similar conclusions are to he drawn as their findings are invariahly low. Our results reported herein confirm these investigators. In the thiocyanate process for chlorine, the presence of HNO_3 in moderate amount does not interfere with the process, but in Mohr's volumetric method for chlorine, the solution should be neutral. Shutt and Carlton (7) have also modified the thiocyanate process for chloride .

Linossier and Lignon (20) attempted to estimate chlorine as chloride by using $HgNO_3$ solution as the precipitant and the resulting insoluble HgCl or calomel weighed. This method was tried out, using their process and also a modified method. The sample used was KCl of known purity which was dissolved in water and precipitated with $HgNO_3$ solution as HgCl. The HgCl was filtered in a weighed crucible of the Gooch type. Some of the samples were

washed with alcohol and dried in a dessicator while others were dried to constant weight at 105°. All results obtained were on the average about one per cent. lower than theoretical, no matter in which manner the HgCl was dried before weighing; nor in this respect did it make much difference as to the weight of the sample taken for analysis.

(To be Continued).

GENERAL NOTES.

ROYAL SOCIETY—PROPOSED NEW OFFICERS.

The following is a list of those recommended by the President and Council of the Royal Society for election to the Council at the anniversary meeting on December 1:—

President.—Sir Charles Sherrington.

Treasurer.—Sir David Prain.

Secretaries.—Mr. W. B. Hardy and Mr. J. H. Jeans.

Foreign Secretary.—Sir Richard Glazebrook.

Other members of the Council.—Sir Frederick Andrewes, Professor J. H. Ashworth, Dr. F. W. Aston, Sir William Bragg, Professor S. Chapman, Sir Dugald Clerk, Dr. H. H. Dale, Professor F. G. Donnan, Professor A. S. Eddington, Professor J. B. Leathes, Dr. G. C. Simpson, Professor J. F. Thorpe, Professor F. E. Weiss, and Professor T. R. Merton.

Lord Crawford and Sir Otto Beit have been elected Fellows of the Society under the Statute which permits of elections on the grounds of conspicuous services rendered to science.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

The Report for the Session 1923-24 contains the Presidential Address and the Memoirs and Proceedings of the Session.

TAR AND TAR PRODUCTS IN GERMANY.

The Commercial Secretary at Cologne (Mr. C. J. Kavanagh) informs the Department of Overseas Trade that according to the "Deutsche Bergwerks Zeitung" of 29th October, business in tar products has notably revived since September. The cause lies unfortunately in the fact that the production of raw tar has considerably decreased and consequently those tar distilleries which must buy the raw material are throwing themselves in large numbers upon those producers which are not bound by working-up contracts and are able to sell raw tar freely. The prices have been increased from 3.50 Mks. per 100 kg. to 5.50 Mks. and even 6 Mks. and more. How it is possible to make a paying business in finished tar products with such prices is difficult to see, since the prices for finished products have not increased but rather fallen.

Assuming the distillation costs to be at least one third of the raw tar price, it is difficult to calculate how the cheaper prices of the finished goods allow of a higher price of raw material.

In East, Central, and South Germany pitch stocks are completely sold out. In the Ruhr district there are still certain stocks, but the quantity, we are informed from a reliable source, will not influence the price development. In view of the large consumption of the briquette works during the last few weeks these amounts have considerably decreased and will probably be disposed of by the end of the year if the pit coal briquettes continue to be sold to the extent by the Coal Syndicate.

The oil production is entirely absorbed by the consumers, so that there are only such stocks as have to be maintained in order to keep up a regular manufacture. In naphthaline in various qualities business is quiet. For anthracene, as used by the chemical industry for dyes, the demand is very brisk and even exceeds the amounts produced.

PROFITS IN THE RETAIL COAL TRADE.

In fulfilment of an undertaking already given to the Public and the Press, the following statement has been received for publication from Mr. George Gentry, Secretary of the Coal Merchants' Federation of Great Britain.

The statement, which is certified by Messrs. D. W. Coates, West, Grimwood & Co., Chartered Accountants, refers to the

six London merchants who met Mr. Shinwell in March last and whose average net profits for the financial years 1921-22 and 1922-23 have already been published.

"We have had produced to us statements, certified in each case by the Auditors, of the profits and tonnage for the year 1923-24 of the companies and firms whose figures for 1921-22 and 1922-23 were reflected in our certificate dated 1st May, 1924.

"We have calculated from the statements the average net profit per ton and certify it to be 1/7.14d.

"The dates to which the accounts are made up vary from 31st March to 30th June.

"The figures are well shewn on a comparable basis, income from investments and wagon-earnings (which are derived from charges at the same tonnage rates as in the two preceding years) being excluded, and no charge being made for interest on capital, remuneration of partners, directors or managing directors, income tax or corporation profits tax."

D. W. COATES, WEST, GRIMWOOD & Co.
3rd November, 1924.

BATTERSEA (LONDON) POLYTECHNIC UNIVERSITY EXAMINATION RESULTS.

	1913-14	1918-19	1919-20	1920-21	1921-22	1922-23	1923-24
D.Sc.	—	—	—	—	—	—	1
Ph.D.	—	—	—	—	—	2	5
M.Sc.	—	—	—	1	1	2	9
M.Sc. (Eng.)	—	—	—	—	—	1	1
B.Sc. Hons.:							
1st Class	—	—	1	6	9	5	2
2nd ,, ...	2	1	1	3	4	5	5
3rd ,, ...	4	1	4	—	5	—	1
B.Sc. Eng. Hons.:							
1st Class	1	1	—	5	7	6	5
2nd ,, ...	3	—	7	9	7	7	4
B.Sc. War Degree ...	—	1	1	1	—	—	—
B.Sc. Pass	6	1	1	—	3	3	3
B.Sc. Eng. Pass ...	1	—	12	11	21	21	7
Inter. Science	11	8	18	18	20	14	12
Inter. Eng.	5	18	26	39	29	16	12
Inter. Arts	1	—	—	—	1	—	1
Durham, 1st Exam. for Mus. Bac.	—	—	—	1	—	—	—
	34	31	71	94	107	81	68
Matriculation	17	13	22	47	21	18	18

DYESTUFFS (IMPORT REGULATION) ACT, 1920.

APPLICATION FOR LICENCES IN OCTOBER, 1924.

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during October has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee.

The total number of applications received during the month was 543, of which 452 were from merchants or importers. To these should be added 25 cases outstanding on the 1st October, making a total for the month of 568. These were dealt with as follow:—

Granted—424 (of which 378 were dealt with within seven days of receipt).

Referred to British makers of similar products—96 (of which 73 were dealt with within seven days of receipt),

Referred to Reparation Supplies available—36 (all dealt with within two days of receipt).

Outstanding on 31st October, 1924—12.

Of the total of 563 applications received, 487, or 86 per cent., were dealt with within seven days of receipt.

UNITED STATES DEPARTMENT OF AGRICULURE.

Cumin Seed.

The following revised and amended definition and standard for cumin seed was adopted by the Joint Committee on Definitions and Standards, composed of representatives of the United States Department of Agriculture, the Association of American Dairy, Food and Drug Officials, and the Association of Official Agricultural Chemists, February 27, 1924:

Cumin Seed is the dried fruit of *Cuminum cyminum* L. It contains not more than nine and five-tenths per cent. (9.5%) of total ash, not more than one and five-tenths per cent. (1.5%) of ash insoluble in hydrochloric acid, nor more than five per cent. (5%) of harmless foreign matter.

The foregoing definition and standard is adopted as a guide for the officials of this department in enforcing the Food and Drugs Act.

Vinegar.

The following revised and amended definition and standard for cider vinegar was adopted by the Joint Committee on Definitions and Standards, composed of representatives of the United States Department of Agriculture, the Association of American Dairy, Food and Drug Officials, and the Association of Official Agricultural Chemists, August 10, 1923:

1. Vinegar, Cider Vinegar, Apple Vinegar, is the product made by the alcoholic and subsequent acetous fermentations of the juice of apples, and contains in one hundred cubic centimeters (100 cc. 20° C.) not less than four (4) grams of acetic acid.

The foregoing definition and standard is adopted as a guide for the officials of this department in enforcing the Food and Drugs Act.

Marjoram, Leaf Marjoram.

The following revised and amended definition and standard for marjoram, leaf marjoram, was adopted by the Joint Committee on Definitions and Standards, composed of representatives of the United States Department of Agriculture, the Association of American Dairy, Food and Drug Officials, and the Association of Official Agricultural Chemists, February 27, 1924:

Marjoram, Leaf Marjoram, is the dried leaves, with or without a small proportion of the flowering tops, of the *Marjorana hortensis Moench*. It contains not more than sixteen per cent. (16%) of total ash, not more than four and five-tenths per cent. (4.5%) of ash insoluble in hydrochloric acid, nor more than ten per cent. (10%) of stems and harmless foreign material.

The foregoing definition and standard is adopted as a guide for the officials of this department in enforcing the Food and Drugs Act.

BOARD OF TRADE ANNOUNCEMENT.

The New Belgian Customs Tariff.

A Translation of the new Belgian Customs Tariff, showing the rates of duty payable as from November 10th on British goods exported to Belgium, will be published as a special Supplement with the "Board of Trade Journal" on Thursday.

RAMSAY MEMORIAL LABORATORY OPENED.

The Ramsay Memorial of Chemical Engineering was opened on the 12th inst., at University College, London, by Prince Arthur of Connaught.

Sir Robert Robertson, Chairman of the Chemical Engineering Sub-Committee, presided. He said there was a want in this country of men with the technical training of chemists who were capable of transferring a laboratory operation to a large scale. Dealing with the details of training, he referred to a practice existing in the United States of taking students to works, and urged chemical manufacturers in this country to consider whether they could not afford similar facilities.

KALAZANA: WULFING.

Chemically, Kalzana is a double salt of calcium lactate and sodium lactate, to which are added palatable adjuvants. It is supplied in tablet form, each tablet containing 7½ grains of Calcoum-Sodium-Lactate.

Considered from the physiological standpoint, Kalzana acts generally as a regenerator of all vegetable and animal cells. Kalazana is said to be an efficient therapeutic agent in many abnormal conditions.

(Indian Medical Record).

INSURANCE COMPANIES INQUIRY.

The Committee recently appointed by the President of the Board of Trade to inquire and report upon the working of the Assurance Companies Act, 1909, held a preliminary sitting at the Board of Trade offices last week, under the chairmanship of Mr. A. C. Clausou, K.C. The Committee decided that for the present they would meet weekly, and that the first oral evidence should be taken at the next sitting, and that the proceedings should be conducted in private. Applications to be heard as witnesses and any general communications upon the subject of the inquiry would be addressed to the secretary, Mr. Walter J. Smith, Board of Trade, Great George Street, London, S.W.1.

ROYAL SOCIETY AWARDS.

The following awards have been made:—

A Royal medal to Sir Dugald Clerk, K.B.E., F.R.S., for his application of scientific principles to engineering problems, particularly to the development of the internal-combustion engine.

A Royal medal to Dr. H. H. Dale, F.R.S., for his researches in pharmacology and physiology.

The Copley medal to Sir E. Sharpey-Schafer, F.R.S., for his valuable work in physiology and histology.

The Rumford medal to Mr. C. V. Boys, F.R.S., for his invention of the gas calorimeter.

The Davy medal to Professor A. G. Perkin, F.R.S., for his researches on the structure of natural colouring matters.

The Darwin medal to Professor T. H. Morgan, Foreign Member R.S., for his valuable work in zoology, especially his researches on heredity and cytology.

NETHERLANDS CALL FOR TENDERS.

The Commercial Secretary of The Hague (Mr. R. V. Laming, O.B.E.) informs the Department of Overseas Trade that the Director of the State Magazine for Medicinal Preparations is inviting tenders, on behalf of the Netherlands Indies Admiistration, for a wide range of drugs and hospital goods.

Tenders, on a proper form, must reach the above Institution not later than 1 p.m. on 2nd December.

Tenders by British firms must be made through their representatives, who must have their permanent address within the Kingdom of the Netherlands, and must further return the names of two guarantors, partners of the same firm not being eligible to act as such.

Copy of the schedule, conditions of tender, etc. (in Dutch) are available for inspection by interested United Kingdom firms on application to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.

HEAT INSULATION.

The Food Investigation Board of the Department of Scientific and Industrial Research have issued a revised edition of their Report on Heat Insulation published in 1921.

The results of experiments carried out at the National Physical Laboratory on the thermal conductivity of the insulating materials usually employed in cold stores are given, and the conclusions arrived at in regard to each of the heat insulators tested are set out in detail. The design of an apparatus by the aid of which thermal conductivity can be determined in absolute measure is also fully described in the Report.

The Battersea Polytechnic has issued, in connection with the Annual Prize Distribution, a Report on the Work of the Session 1923-4. The work done in the Chemistry Department is on a very high level and the successes gained at University Examinations are very creditable indeed.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE ROYAL SOCIETY.

Thursday, November 13, 1924, at 4.30 p.m. Papers read:—

N. K. Adam and J. W. W. Dyer—*The Molecular Structure of Thin Films. Part VI.* Communicated by W. B. Hardy, Sec. R.S.

T. Alty — *The Cataphoresis of Gas Bubbles in Water.* Communicated by Sir Joseph Thomson, F.R.S.

Papers read in title only:—

D. R. Hartree—*Some Relations between the Optical Spectra of Different Atoms of the same Electron Structure. I—Lithium-like and Sodium-like Atoms.* Communicated by Sir Ernest Rutherford, F.R.S.

P. A. M. Dirac — *The Conditions for Statistical Equilibrium between Atoms, Electrons and Radiation.* Communicated by Sir Ernest Rutherford, F.R.S.

Ida Doubleday—*Boundary Lubrication. Further Consideration of the Influence of the Composition of the Solid Face.* Communicated by W. B. Hardy, Sec. R.S.

Chaistina C. Miller — *The Stokes-Einstein Law for Diffusion in Solution.* Communicated by Sir James Walker, F.R.S.

Helen S. French and T. M. Lowry, F.R.S.—*Studies of Co-ordination. Part I—Absorption Spectra and Co-ordination of some Cupric Compounds.*

L. F. Bates—*On the Range of α-Particles in Rare Gases.* Communicated by Sir Ernest Rutherford, F.R.S.

D. H. Black—*The β-Ray Spectrum of Mesothorium 2.* Communicated by Sir Ernest Rutherford, F.R.S.

J. Keith Roberts—*The Thermal Expansion of Crystals of Metallic Bismuth.* Communicated by Sir Joseph Petavel, F.R.S.

R. Stonely—*Elastic Waves at the Surface of Separation of Two Solids.* Communicated by Prof. H. F. Baker, F.R.S.

ROYAL SOCIETY OF ARTS.

Peter Le Neve Foster Prize.

Under the Peter Le Neve Foster Trust the Council offer a Prize of £25 for an essay on "The Effect of Trade Union Regulations on Industrial Output."

Intending competitors must send in their essays not later than March 31st, 1925, to the Secretary, Royal Society of Arts, John Street, Adelphi, London, W.C.2.

The essays must be typed or clearly written. They may be sent in under the author's name, or under a motto, accompanied by a sealed envelope enclosing the name, as preferred.

The judges will be appointed by the Council.

The Council reserve the right of withholding the Prize or of awarding a smaller Prize or smaller Prizes, if in the opinion of the judges nothing deserving the full award is submitted.

SOCIETY OF PUBLIC ANALYSTS.

Ordinary Meeting.

Held at the Chemical Society's Rooms, Burlington House, on Wednesday, 5th November, 1924. Mr. G. Rudd Thompson, President, was in the chair.

Certificates were read for the first time in favour of: — Messrs. Arthur Chapman Barnes, B.Sc., F.I.C.; John Jacob Fox, D.Sc. (Lond.), F.I.C.; Thomas Congalton Hay; Harold Rupert Jensen, M.Sc. (Liv.), A.I.C.

Certificates were read for the second time in favour of:—Messrs. Arthur Cecil Brooks, A.R.C.Sc.I., A.I.C.; William Donovan, M.Sc. (New Zealand); Albert George Flower, B.Sc. (Lond.); Clifford Hollingsworth, F.I.C.; George Marshall Norman, B.Sc. (Lond.), A.R.C.S., F.I.C.; Charles Edward Sage, F.I.C.; Percy Frank Spendlove, B.Sc., A.R.C.S., A.I.C.; Charles William Spiers, M.Sc. (Bristol), A.I.C.; Leslie Herbert Trace, A.I.C., B.Sc. (Lond.); James Rawson Walmsley, A.M.S.T., F.I.C.

The following were elected Members of the Society:—Messrs. John Ernst Nyrop, Cand. Polyt. (Copenhagen University); Clifford Padgett Thorpe, B.Sc. (Manch.).

The following papers were read:

"On certain new Methods for the Estimation of Arsenic and its Occurrence in Fish and Urine," by H. E. Cox, M.Sc., Ph.D., F.I.C.

"The Estimation of Cadmium in Brass," by A. T. Etheridge, M.B.E., B.Sc., F.I.C.

"The 'Hoyberg' Method of Milk and Cream Testing," by N. C. Wright, B.A., and J. Golding, D.S.O., F.I.C.

"An Apparatus for the Catalytic Dehydrogenation of Alcohols," by S. G. Willimott, Ph.D., B.Sc.

On Certain New Methods for the Estimation of Small Quantities of Arsenic and its Occurrence in Urine and in Fish, by H. E. Cox, Ph.D., M.Sc., F.I.C.

The methods and results of the Swedish Commission on chronic arsenical poisoning have been carefully tested and the conclusion reached that the nitric and sulphuric acid digestion process described by Bang and Ramberg gives higher and more accurate results than the older wet combustion method adopted by the Joint Committee of the Society of Public Analysts and the Society of Chemical Industry in 1902. The iodine titration method of Bang is not reliable, but Ramberg's bromate method gives satisfactory results if the amount of arsenious oxide to be estimated is not less that 0.01 mgrm; below this amount the Marsh-Berzelius process following Ramberg's method of destruction is preferable. It is found that normal urine may contain quantities of arsenic which have been thought to be associated only with chronic arsenical poisoning; amounts present in the urie of persons on known diets varied from 0.0 up to 0.58 mgrm per litre. Large excretion of arsenic is due to the eating of fish, and it is shown that fish, specially plaice, may contain arsenic up to 3 parts per million. The eating of such fish leads to the appearance of arsenic in the urine within twenty-four hours.

Estimation of Cadmium in Brass, by A. T. Etheridge, M.B.E., B.Sc., Ph.D., F.I.C.

The preliminary electrolytic separation of copper and lead is effected as described by the author (*Analyst*, 1924, 49, 371). The liquid containing cadmium, zinc and other metals is treated with sulphuretted hydrogen in acid solution, sulphides are taken up, precipitated next in alkaline solution, and again treated as before in both solid and alkaline solution, and a final acid precipitation then leaves pure cadmium sulphide which is weighed after conversion into sulphate. Though the method is tedious, the purity of the product is ensured with great accuracy within 0.05% cadmium in brass.

The 'Hoyberg' Method of Cream and Milk Testing, by N. C. Wright, B.A., and J. Golding, D.S.O., F.I.C.

The "Hoyberg" Method for determination of fat in milk and cream has been tested under carefully controlled conditions against gravimetric estimations. For milk testing the method has been found to give low and variable results, and to be unreliable for routine estimations, particularly in the hands of unskilled workers, for whose use it is chiefly designed. For cream testing the results show a greater degree of accuracy, the errors being chiefly due to the fact that the cream is measured by volume and not by weight.

An Apparatus for the Catalytic Dehydrogenation of Alcohols, by Stanley G. Willimott, Ph.D., B.Sc.

The usual laboratory methods for the preparation of aliphatic aldehydes are shown to be unsatisfactory. An improved dehydrogenation apparatus is described, the chief advantages being:—(a) The quantity of alcohol vapour entering the dehydrogenation tube is controlled by regulation of the boiling. The vapour passes through a heated copper spiral, and entering the tube at 300° C. is readily dehydrogenated by the copper catalyst. (b) The introduction of the preheater prevents liquid entering the tube with consequent cracking. (c) Heating of the air-bath is facilitated by employing an ordinary combustion furnace; asbestos sheeting maintains the temperature uniform.

THE CHEMICAL SOCIETY.

Papers read at the Ordinary Scientific Meeting, Nov. 6th.

Investigations on the dependence of rota-

tory power on chemical constitution. Part XXIV. Further experiments on the Walden inversion, by J. KENYON, H. PHILLIPS, and H. G. TURLEY.

Lævorotatory lactic acid, which may be assumed to have a lævo-configuration, when esterified gives dextorotatory ethyl lactate. This ester readily yields a *p*-toluenesul phonyl derivative from which dextrorotatory ethyl α-benzoxypropionate can be prepared by interaction with potassium benzoate, whereas, by the action of benzoyl chloride on the same sample of dextrorotatory ethyl lactate, lævorotatory ethyl α-benzoxypropionate is obtained. A complete inversion of *l*-lactic acid is indicated in the first case. Similarly dextrorotatory α-bromopropionic ester has been obtained by the interaction of the lævorotatory sulphonic ester with Grignard reagents. This reaction has an important bearing on the relative configurations of *l*-lactic acid and dextroratatory α-bromopropionic acid and therefore on the theoretical aspect of the Walden inversion.

The Mechanism of the Walden Inversion, by T. M. LOWRY.

A mechanism, based upon the explanation of Gadamer, is proposed, in which each step represents a process already suggested and used for other purposes before being applied to the Walden inversion.

A spectroscopic study of the luminescent oxidation of phosphorous, by H. J. EMELEUS and W. E. DOWNEY.

A spectroscopic examination of the light emitted when phosphorous burns has given the following results. When phosphorous burns in enriched air with a flame temperature of 800°, it shows five broad bands in the ultra-violet portion of the spectrum. Phosphorus burning in air under reduced pressure with a flame temperature of 125° emits five groups of narrow bands. The groups occupy the same positions as the bands obtained with the hot flame. Glowing phosphorus emits the same groups of narrow bands. This latter result contradicts Petrikaln's recent work but agrees with the earlier work of Centnerszwer and Petrikaln.

The adsorption of catalytically poisonous metals by platinum. Part I. The adsorption of lead and mercury, by E. B. MAXTED.

The adsorption of lead and of mercury from dilute aqueous solutions of their salts has been studied, with the ultimate object of finding the variation in the activity of a platinum catalyst with the actual concentration of such inhabitants on its surface. In these adsorption measurements it was found, both for lead and for mercury, that the adsorbed concentration is directly proportional to the bulk concentration up to a region in the neighbourhood of the complete saturation of the surface of the platinum by the substance adsorbed. With the platinum employed, saturation was obtained with about 27 mg. of lead and about 8 mg. of mercury per gram of platinum. From the results obtained, it would appear that the activity of a platinum catalyst in the presence of such inhahitants is a linear function of the concentration of the poison on its surface.

THE INSTITUTION OF ELECTRICAL ENGINEERS.

The Ordinary Meeting was held in the Lecture Theatre of the Institution, Savoy Place, Victoria Embankment, W.C.2., on Thursday, 20th November, at 6 p.m.

Paper read:

Automatic and Semi-Automatic Mercury-Bapour Rectifier Substations, by MR. GOGERS.

A meeting of the Society of Glass Technology was held in the Lecture Theatre of the Department of Coal, Gas and Fuel Industries, The University, Leeds, on Wednesday, November 19th, at 3 p.m.

AGENDA.

A Note on the Glass Houses of the Leeds District, in the 17th, 18th and early 19th Centuries, by FRANCIS BUCKLEY, ESQ.

A Striking Instance of Fireclay Corrosion through the action of Saltcake, by PROF. W. E. S. TURNER, D.Sc.

A Note on Some Properties of a Sandstone Block after Use in a Glass Furnace, by H. S. HOULDSWORTH, M.Sc.

The Production of Colourless Glass in Tank Furnaces, with Special Reference to the Use of Selenium, Part IV. The Influence of Arsenious Oxide, by A. COESEN, M.Sc., and PROF. W. E. S. TURNER, D.Sc.

PHYSICAL SOCIETY OF LONDON.

Nov. 14.

A Demonstration of an "Electrical Method of Synthesising Vowel Sounds" was given by Dr. W. H. Eccles, F.R.S.

Papers read:—

The Dielectric Properties of Mica, by D. W. Dye, B.Sc., and L. Hartshorn, B.Sc., D.I.C., The National Physical Laboratory.

The X-ray Emission of Electrons from Metal Films, with Special Reference to the Region of the Absorption Limit, by Dr. Lewis Simons, Birkbeck College, London.

Oct. 24. F. E. Smith, C.B.E., F.R.S., in the chair.

Underblown Pipes, by D. Gunnaiya, M.A., by Mr. D. J. Blaikley, who also gave a Demonstration.

The phenomena of underblown pipes have been studied in the case of four wooden pipes ranging over an octave. It has been found that they present many features of remarkable interest. The existing theories regarding the phenomena have been discussed, and a new theory is proposed which attempts at once to explain both these phenomena.

The Temperature Gradient in Gases at Various Pressures, by W. Mandell, B.Sc., and J. West, B.Sc.

A careful re-examination of the problem of the temperature gradients through gases at various pressures has been attempted.

Sets of curves indicating these gradients at various pressures and other interesting relations were obtained. Amongst other features, they show quite definitely the existence in contact with the vessel walls—at low pressures—of very large "temperature jumps."

An attempt to explain the general character of the results is based on the assumption of the presence at the walls, of a gas film possessing certain properties due to the attracting forces existing amongst wall molecules and gas molecules.

Instead of using one thermocouple only to determine the temperature at any point in the enclosure, severa thermocouples of differing thicknesses—and therefore differing curvature—were employed under identical conditions. Systematic differences amoigst corresponding readings of the thermocouples were noticed. These may also be attributed to the presence round the various thermocouples of gas films whose thickness and character vary with the thickness of the couple.

Vectorial Dimensions, by J. F. S. Ross. M.C., B.Sc., Assoc.M.Inst.C.E.

THE FARADAY SOCIETY.

A general discussion on "The Physical Chemistry of Igneous Rock Formation," was held jointly with the Geological Society and the Mineralogical Society, on Oct. 22. The following papers were read:—

Homogeneous Equilibria in Magmatic Melts and their Bearing on the Processes of Igneous Rock-formation, by Paul Niggli (Zurich).

The petrologist engaged in the study of igneous rocks has before him the products of immense natural processes. He knows that in spite of many and great complications, the laws of physical-chemistry that experimental investigation has taught him, regulated the formation of the magmatic mineral deposits, and is thus conscious of the fact that his researches are largely applied physical chemistry in the great natural laboratory of the earth. For him the magmatic solutions contained in the earth's crust are the physical-chemical systems whose behaviour under vario us conditions he has to unravel.

A consideration of the homogeneous equilibria in the magma, enables us to find a simple expression for the physical chemical causes from which the different chief associations of igneous rocks proceed.

If geotectonic conditions be responsible for the particular trend taken by any process of differentiation, their efficacy must primarily depend on the influence which geological factors are capable of exerting on the conditions of equilibrium. The nature and extent of the dependence of homogeneous equilibria on geological factors must therefore be made the subject of increased research. Importance also attaches to the clear recognition of the fact that the differences between the magmatic constitution of the various types of province are merely of a gradual nature. This being so, no surprise will be felt if cases of transition or commingly arise. Any magma can, if subjected to special conditions, depart from its original tribal characteristics and give rise to an altered process of differentiation.

It is an undertaking of peculiar interest to trace among the external actors the causes of much mutations, and thus to collect new information concerning the influencing of the equilibria.

But the study of homogeneous equilibria is also of the greatest value for the systematic treatment of the products of magmatic consolidation. It shows clearly how necessary it is to separate a Mediterranean rock-association, in which desilicification chiefly affects the comparatively unstable potash felspar molecule, from the Atlantic group. The rational classification of rock-types can only be carried through if the stability of the various molecules in the melt be constantly kept in view. Thus it serves no useful pjurpose to use the presence or absence of olivine as a main criterion in classification. We have seen that the more highly silicified minerals can be disilicified with the greatest ease, and once formed olivine will according to circumstances, be removed by resorption or remain present as such. Or again, why should leucite-bearing rocks be placed far apart from their heteromorphic equivalents, when the formation of leucite is so largely dependent on external factors?

Some Ultimate Problems in Petrogenesis, by W. Alfred Richardson, B.Sc. (Eng.), B.A., D.Sc., F.G.A. A.M.I.-Min.E.

The science of petrogenisis took its origin and found its first problems in the recognition of affinities shown by rocks associated in the field, in such facts as the existence of petrographic provinces and diaschistic dykes. Realising that ultimately problems of origin lead back to theories of cosmogeny most petrologists, in this country at any rate, restricted themselves to considering how on the postulate of a local source of magma the varieties and distribution of rocks in a given area could have arisen.

Since in its earlier stages petrology consisted of a vast mass of descriptive data, it is clear that it was not only wise to limit the problems to definite areas, but that it was the only way to bring the accumulated material into order. On the other hand, this limitation has not been without its dangers; and in particular it has lead to an over emphasis of the problem of the origin of the more highly specialised rock types.

The chief needs of research on the questions raised were mentioned and included.

The tabulation of the areas and exposed volumes of visible igneous rocks, so that further estimates of relative volumes could be made. This tabulation could conveniently be made by official surveys at the end of their sheet memoirs, for the values are best calculated from the large scale manuscript maps and the field notes of the surveyors.

The systematic sampling of rock masses for chemical analysis. This again is best undertaken by official surveys. The expense and difficulty of obtainig complete chemical analyses raises the question as to whether a larger number of incomplete analyses from large masses would not serve many purposes better than the present custom of complete and elaborate analyses on isolated specimens.

There is great need of investigations on the behaviour of silicate systems in the presence of vapour phases.

Need is also felt especially in relation to the thermal problems of petrology for more accurate and systematic determination of the temparature gradients, and of the geographical distribution of the gradients.

In vie of many conflicting analyses of the thermal state of the earth especially the upper crust, organised research into the whole question is required both from the standpoint of geophysics and petrology.

(*To be Continued.*)

CORRESPONDENCE.

THE ATOM.

To the Editor of The Chemical News.

Sir,—In reply to Mr. Loring's request that I would explain how a part of an atom can have no volume, I would like to draw his attention to the article on vanadium in the *Chemical News*, 1924, CXXVIII., 101. The Law of Relative Volume was first given there and in the following paragraphs his question was answered in anticipation, and also illustrated by means of experimental facts.

Again in the paper on oxygen, 1924, CXXVIII., 230, the following remark was made:—" It is evident that neutral oxygen is formed from acidic oxygen by the complete absorption of the two helium portions by the metallic part of the element." A similar remark was made in the next paper on sulphur.

The complete absorption of a portion of a body by the remainder is a common occurrence in nature. E.g., when a snail of volume 2 cc. and of average density 1.5 decides to throw out a horn, its total volume might become 2.2 cc., whilst its average density might decrease to 1.4. When it withdraws the horn, the volume 0.2 disappears entirely, because it is absorbed by the volume of its body which can easily be understood to remain constant whilst varying in density. Of course the horn has a volume inside the body of a snail, but it has disappeared entirely as far as the external world is concerned.

I trust that Mr. Loring will agree now that there is no paradox in the matter.

Yours, etc.,

HAWKSWORTH COLLINS.

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

26012—Asseev, C. — Production of aluminium compounds. Oct. 31st.

Abstract Published This Week.

220985—Artificial resins, varnishes.— Karpen & Bros., S., 678, West 22nd Street, Chicago, U.S.A.

Phenol-methylene condensation products are produced by heating an aldehyde dichloride with a phenol in the presence of ammonia, the proportions of the aldehyde dichloride and phenolic being being such that approximately 1.5 phenolic groups are present for each methylene group. The aldehyde dichloride used is generally methylene chloride, but ethylidene and propyliammonio, the proportions of the aldehyde dene chlorides may also be employed. The ammonia is preferably present in excess; compounds of ammonia, such as methylamine or ammonium carbonate, may replace the ammonia. Phenol cresols and naphthols are mentioned as suitable phenolic bodies. The fusible, soluble resin formed by the condensation is washed with water to remove the ammonium chloride, excess of phenol then eliminated by boiling or by blowing air through the heated resin, and finally a hardening agent, such as hexamethylene-tetramine or formaldehyde or chloride with a phenol in the presence of dichloride and phenolic body being such and the product converted by heat into the insoluble and infusible product. Fibrous or other fillers may be incorporated in the resin at any stage. Specifications 9291/14, 119,253, and 196,265 are referred to.

Aldehyde dichlorides are obtained as byproducts in the preparation of methyl chloride by chlorinating methane or natural gas.

Varnishes are prepared by dissolving the fusible, soluble resin in a solvent and adding sufficient hexamethylenetetramine or other hardening agent to effect the conversion to the final infusible and practically insoluble stage.

221716—Casin compounds.—Soc. of Chemical Industry in Basle; Basle, Switzerland.

The organic phosphorus compound contained in milk casein is obtained free from mineral phosphates by digestion in weakly alkaline solution with pancreatic ferments, precipitating the filtered liquid by means of a heavy metal salt, dissolving the precipitated heavy metal salt in alkali carbonate solution, thereby leaving the mineral phosphate, precipitating the alkali metal salt with alcohol and re-dissolving it in water, again precipitating by means of a heavy metal salt and removing the heavy metal such as by means of hydrogen sulphide, and finally precipitating the free acid with alcohol and drying. The alkali carbonate solution may if desired be subjected to a second digestion with pancreatic ferments prior to the precipitation by alcohol. In an example commercial milk casein is suspended in hot water and anhydrous sodium carbonate, sodium bicarbonate, trypsin of pancreas, and toluene added. The filtered liquid is precipitated with sugar of lead and basic lead acetate solution. The precipitate is dissolved in sodium carbonate until slightly alkaline to phenolpthalein and the solution separated from lead phosphate and carbonate. A second digestion with trypsin may follow, and the phosphorus compound is further purified as described above, lead again being used as the heavy metal. Copper acetate or a mercury salt may also be employed as a precipitant. The alkali metal or alkaline earth salts may be obtained by neutralization of the free acid, and the iron salt by acting on the sodium salt with a soluble iron salt.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for

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THE STRUCTURE OF CHROMIUM.

By HAWKSWORTH COLLINS, B.A. Camb.).

The constitution of an atom of chromium has previously been given in *The Chemical News* as Mg + Si for the following six reasons.

(1) The sum of the atomic weights of Mg (24) and of Si (28) is equal to the atomic weight of Cr (52).

(2) The sum of the valences of the dyad Mg and of the tetrad Si is equal to the valency of the hexad Cr.

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CHEMICAL NEWS, MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

(3) The atomic weight of Cr can be split up (as previously shown in many other cases) into as many parts 39, 23, 7, 3, 1, as the element has valences, and in such a way that the unit can always be put in the even places, the other numbers occupying the odd places in descending order of magnitude:—23 + 1 + 23 + 1 + 3 +1.

If the atomic weight of Cr had been any number but 52 between 49 and 55 inclusive, it would have been impossible to split it up in this way into six portions.

(4) As there is a free helium portion (3 + 1), the element must be a non-metal.

(5) Chromite, an oxide of Fe and Cr, is found in large masses in serpentine, which is an oxide of Mg and Si.

(6) A mass of 23 takes a prominent part in the formation of all elements of greater atomic weight than sodium. (*The Chemical News*, 1920, CXXI., 157)

Therefore Cr = MgSi = Na + H + Na + H + H_3 + H.

This structure will now be proved to be correct quite independently by means of the laws of relative volume and of heat of formation.

TABLE I.

The Relative Volumes of Chromium.

Cr	=	Mg	+	Si
7.13	=	0	+	7.13
8.71	=	8.71	+	0
21.73	=	8.71	+	13.02
7.51	=	7.51	+	0

7.13 and 13.02 were shown to be volumes of silicon in *The Chemical News*, 1924, CXXIX., 47. Also 8.71 and 7.51 were shown to be constituent parts of vanadium, which equals MgAl (*The Chemical News*, 1924, CXXVIII., 101); and in Table II. they are shown to be volumes of Mg itself.

TABLE II.

Experimental Data Illustrating Table 1.

	Relative Volume.	Theor. S.G. at 15° C.	Obs. S.G.
(321)	Cr 7.13	7.3	7.3 Bunsen
(322)	AlCr 9.05 + 7.13	4.9	4.9 Wohler
(323)	Al_2O_3 2(9.05) + 3(2.51)	3.98	3.98 14° Grandeau
(324)	$Al(OH)_3$ 9.05 + 3(2.51 + 5.76)	2.3	2.3 Chem. Kal.
(325)	Cr_2O_3 2(8.71) + 3(2.51)	6.09	6.2 Schiff
			5.21 Wohler
(326)	Cr_2O_3 2(8.71) + 2(2.51) + 4.45	5.65	,, ,,
(327)	Cr_2O_3 2(8.71) + 2.51 + 2(4.45)	5.272	,, ,,
(328)	CrB 8.71 + 2.9	5.4	5.4 17° Nostrand
(329)	MnB_2 6.94 + 2(2.9)	6.04	6.04 19° ,,
(330)	MnSi 6.94 + 7.13	5.90	5.90 15° ,,
(331)	$MnSi_2$ 6.94 + 2(7.13)	5.24	5.24 13° ,,
(332)	Cr_2S_3 2(8.71) + 3(10.51)	4.09	4.092 Playfair
(333)	CrAs 8.71 + 11.38	6.32	6.35 16° Nostrand
(334)	MgO 8.71 + 2.51	3.565	3.5699 0° Ditte
(335)	$MgO.MgCO_3.3H_2O$ 8.71 + 2.51 + 8.71 + 20.55 + 3(14.03)	2.156	2.152 Internatl
(336)	$MgCl_2.6H_2O$ 8.71 + 2(15.085) + 6(14.03)	1.65	1.65 Ochsenius
(337)	CrO_3 21.73 + 7.53 + 4.45 + 2.51	2.76	2.737 14° Ehlers 2.775 Zettnow
	(7.53)		
(338)	CrO_3 21.73 + (2.51) + 4.45 + 2.51	2.97	2.82 Schafarik
(339)	CrO_2Cl_2 21.73 + 7.53 + 4.45 + 2(23.01)	1.94	1.92 25° Thorpe 1.96 0° ,,
(340)	Cr_2Cl_6 2(21.73) + 6(15.085)	2.366	2.36 Chem. Kal.
(341)	$KCr(SO_4)_2 . 12H_2O$ 22.29 + 21.73 + 2(30.59) + 12(14.03)	1.824	1.826 Playfair & J 1.823 16°.5 Spring
(342)	$RbCr(SO_4)_2 . 12H_2O$ 26.57 + 21.73 + 2.(30.59) + 12(14.03)	1.962	1.946 Soret 1.967 17° Petterssn
	(In the four following molecules 35.65 = 21.73 + 2(4.45 + 2.51)		
(343)	Na_2CrO_4 2(11.85) + 35.65	2.73	2.7358 12° Abbott
(344)	K_2CrO_4 2(18.05) + 35.65	2.704	2.705 Kopp
(345)	Ag_2CrO_4 10.25 + 13.29 + 35.65	5.575	5.536 Rettig 5.583 Schroder
(346)	$PbCrO_4$ 17.42 + 35.65	6.07	6.118 Mahross 6.004 Mohs
(347)	Cr_2S_3 21.73 + 8.71 + 2.(15.53) + 10.51	2.78	2.79 10° Schafarik
(348)	$K_2Cr_2O_7$ 2(18.05) + 2(21.73) + 7.53 + 4(4.45) + 2(2.51)	2.675	2.677 Schroder 2.66 15° Stolba
(349)	Cr 7.51	6.92	6.92 20° Nostrand
(350)	Cr_3Si 8.71 + 2(7.51) + 2(7.13)	5.6	5.6 Nostrand
(351)	$Cr_2Ca_3(SiO_4)_3$ 2(7.51) + 3(14.54) + 3(28.08)	3.50	3.5145 Erdmann
(352)	Cr_2Cl_6 2(7.51) + 6(15.085)	3.004	3.03 17° Schafarik
(353)	$MgHPO_4.3H_2O$ 7.51 + 5.76 + 14.56 + 4.45 + 3(2.51) + 3(14.03)	3.124	3.123 15° Nostrand
(354)	$MgCO_3$ 7.51 + 20.55	3.0	3.007 Jenzsch 2.9 - 3.1 Chem. Kal.

TABLE III.

Heat of Formation of Chromium.	Original Volume.		Rel. Vol. in combination at 15° C.		Change of Volume
$-9859 = 120 \times (-1.58) \times 52$	7.13	=	8.71	-	1.58
$-91104 = 120 \times (-14.6) \times 52$	7.13	=	21.73	-	14.6

TABLE IV.

Experimental Data Illustrating Table III.

	H.F.		Theor.	Obs.
Cr_2O_3	$-2(9859) + 3(96155)$	=	268747	267800 cryst
	(corresponds with No. 325, Table II.)			
Cr_2O_3	$-2(9859) + 2(96155) + 71515$	=	344107	243800 amorph.
	(corresponds with No. 326)			
CrO_3	$-91104 + \overset{(32341)}{(96155)} + 71515 + 96155$	=	140814	140000. aq. 141900
	(corresponds with No. 338)			

The only other H.F. available is that of $K_2.Cr_2O_3.O_4$ given as 226440, aq.209740.

If an experiment were made to form potassium bichromate, starting with Cr_2O_3 (No 327, Table II.) in which the volume of Cr is 8.71, the element would have to absorb 81245 calories in order to reach the volume 21.73, for

$$-81245 = 120 \times (-13.02) \times 52, \quad 8.71 = 21.73 - 13.02.$$

This is equivalent to its absorbing $-91104 = -81245 - 9859$ calories in expanding from 7.13 to 21.73. The H.F. of $K_2Cr_2O_7$ is therefore $2(52837) - 2(81245) + 32341 + 2(71515) + 96155 = 214710$. This value lies between the two experimental values given above, and is therefore as near to experiment as can be expected.

The three ogygen atoms in combination with Cr_2 do not alter, so that their volumes remain as $2(4.45) + 2.51$, and the volumes of the four additional oxygen atoms are $7.53 + 2(4.45) + 2.51$. The H.F. of the molecule therefore corresponds with No. 348.

The H.F. 52837 of K will be demonstrated in a future paper on that element.

SUMMARY.

In this proof of the constitution and structure of an atom of chromium (which is most certainly a proof, because it shows the exact *numerical connection between atomic* weight, atomic volume, valency, heat of formation, and mineralogical facts) the following laws and discoveries are illustrated:

The five main principles in the constitution and structure of the chemical elements:

(1) Single chemical valences emanate from elements or portions (of elements) whose masses are 1, 3, 7, 23 and 39.

(2) The non-metallic nature of an element is always due to a pair or pairs of electropositive forces, each pair emanating from a portion of the element, of which the mass is 4, taking the mass of an atom of hydrogen as unit.

This is also called "The Law of the Formation of Non metals."

(3) Monadic Na (23) takes a prominent part in the formation of all elements of greater mass than itself.

(4) In the simpler elements H (1) forms the *connecting* link between the other portions, 3, 7, 23, and 39.

(5) Each of the heavier elements is formed by the union of simpler elements (which are indicated in each case by mineralogical and chemical facts combined).

(6) The Law of Electro-Positive and -Negative Valences:—

Electro-negative forces emanate from the metallic parts of non-metallic elements; all other valences are electro-positive.

(7) The Interrelationship of the Elements (demonstrated fully in the cases of Cr, Mn and V in *The Chemical News*, 1920, CXX., 169).

(8) The discovery of the relative volume of each atom in a molecule, thereby converting the thousands of numerical data of specific gravity into exact *instruments* of research.

(9) The Law of Relative Volume:—The relative volume of an atom is the sum of the relative volumes of its parts, any one or more of which may be zero.

(10) The discovery of the amount of heat of formation which belongs to each atom in a molecule.

(11) The Law of Heat of Formation:—The heat of formation of an element is proportional to the product of the atomic weight and the change of volume; there being two distinct series, the sodium elements and the sub-sodium elements.

CRITICAL STUDIES ON METHODS OF ANALYSIS.

XIV.: Chlorine.

By Leon A. Congdon, W. B. Crabtree, H. W. Coles, L. L. Smith, and M. L. Vehalgo.

(Contribution from the Department of Chemistry, Syracuse University).

(Continued from Page 320).

Experimental.

One series of results was obtained on a sample of KCl of known purity, containing a very faint trace of sodium. These results are tabulated in Table I.

Another series of experiments were tried out on a sample of NH_4Cl of known purity, containing 0.001 % Fe, 0.001 % CaO, 0.001 % SO_3, and 0.001 % non volatile matter. These results are tabulated in Table II.

A study of these tables of results shows that ammonium or potassium chloride salts give similar resuts when tried out by the various methods used with the exception of Mohr's volumetric precipitation method, where the presence of the ammonium radicle seems to give high results. The study of the gravimetric HgCl method on a sample of KCl shows the method to give on the average one per cent. lower results than theoretical. It was found by experiment that it is necessary to filter off the AgCl in the thiocyanate method before titrating for the excess of silver used, since over one half of one present lower theoretical results will be obtained if this is not done.

Table I.

Method Used.	Weight Sample. Gram.	Theor. % Chlorine in Sample.	Amount Chlorine found. %	Average Amount Chlorine found. %	Difference from Theor. %
Gravimetric	0.102	47.58	47.49	47.55	-0.03
as	0.105		47.54		
	0.198		47.53		
AgCl.	0.202		47.58		
	0.300		47.59		
	0.301		47.61		
	0.395		47.50		
	0.402		47.55		
	0.501		47.66		
	0.502		47.39		
	0.601		47.41		
	0.604		47.53		
	0.701		47.58		
	0.702		47.62		
	0.799		47.60		
	0.801				
Gravimetric as HgCl.					
(a) Washed with alcohol and dried in dessicator.	0.103	47.58	46.33	46.54	-1.04
	0.403		46.75		

(b) Dried at 105°.	0.102	47.58	46.42	46.34	-1.24
	0.105		46.27		
	0.107		46.50		
	0.806		46.16		
Mohr's Volumetric Method	0.101	47.58	47.46	47.52	-0.06
	0.101		47.51		
	0.203		47.55		
	0.205		47.48		
	0.506		47.56		
	0.510		47.53		
	0.798		47.46		
	0.802		47.57		
Thiocyanate Voumetric Method. (Filtering off AgCl ppte.)	0.0642	47.58	47.56	47.48	-0.10
	0.0755		47.39		

TABLE II.

Method Used.	Weight Sample. Gram.	Theor. % Chlorine in Sample.	Amount Chlorine found. %	Average Amount Chlorine found. %	Difference from Theor. %
Gravimetric	0.0839	66.29	66.43	66.31	+0.02
	0.1234		66.14		
as	0.1735		66.12		
	0.2960		66.43		
AgCl.	0.2964		66.38		
	0.3000		66.53		
	0.3553		66.28		
	0.3759		66.30		
Mohr's Volumetric Method.	0.1448	66.29	67.13	69.93	+0.64
	0.1469		65.87		
	0.1520		67.80		
	0.1549		67.28		
	0.1555		67.26		
	0.1579		67.02		
	0.1612		66.47		
	0.1743		67.29		
	0.2138		66.50		
Thiocyanate Volumetric Method. (a) Net filtering off the AgCl.)	0.0867	66.29	66.05	65.77	-0.52
	0.0898		65.29		
	0.0957		65.82		
	0.0984		65.97		
(b) Filtering off the AgCl).	0.05	66.29	65.58	66.14	-0.15
	0.05		66.09		
	0.05		66.20		
	0.05		66.67		

Summary and Conclusions.

1. A general survey of the literature is given on the estimation of chlorine.

2. Six methods and modifications for the determination of chlorine as chloride were experimentally performed on two chlorides of nown purity, the accuracy of which are as follows in order names:—Gay Lussac's gravimetric AgCl precipitation method; Mohr's volumetric K_2CrO_4 indicator $AgNO_3$ precipitation method (in absence of interfering salts, acids, etc.); Indirect Volumetric Thiocyanate, $AgNO_3$, ferric alum indicator, precipitation method (first filtering off the AgCl); Indirect volumetric Thiocyanate, $AgNO_3$, *ferric alum indicator*, precipitation method (not filtering off the AgCl); Mohr's volumetric K_2CrO_4 indicator, $AgNO_3$ precipitation method (in presence of ammonium salts); and Linossier's and Lignon's gravimetric method as HgCl.

3. The use of Linossier and Lignon's gravimetric method as HgCl for a soluble chloride can be put into general practice, provided the result obtained is considered to be less than that actually present. The correct percentage may be obtained by multiplying the result obtained by the factor, 0.976.

4. Mohr's volumetric method for chlorides in neutral solution was found to be quite accurate, except when ammonium salts of chlorine were determineed. The presence of the ammonium salt gave higher results than theoretical.

5. It was found that in the thiocyanate volumetric process for chlorine there is a necessity of first filtering off the AgCl precipitate before determining the excess of silver by the thiocyanate method. If this is not done, appreciable lower results will be obtained.

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General Notes.

FRACTIONAL HORSE-POWER MOTORS: A BRITISH ACHIEVEMENT.

The Board of Trade Journal states that before the war the manufacture of fractional horse-power motors was almost exclusively a Continental and American enterprise, and the British market usually satisfied its needs from foreign sources. Within the last few years there has developed, however, a British industry which has already succeeded in capturing a large part of the home market for these motors and looks forward to a substantial overseas trade in the near future.

The applications of the electric motor of fractional horse-power are many and various; sewing machines, vacuum cleaners, washers, machine tools, letter copiers; these and a hundred others used in the home, workshop, or office are being driven by motors of small size of one-fourtieth h.p. upwards.

ROYAL INSTITUTION.

A General Meeting of the members of the Royal Institution was held on Monday afternoon, November 3, Sir James Crichton-Browne, Treasurer and Vice-President, in the chair.

The special thanks of the members were returned to Sir Alfred Yarrow for his generous donation towards the cost of advertising the lectures, and to Mr. Archibald D. Fox for his gift of Michael Faraday's Penknife.

The Chairman announced that the Christmas Lectures this year would be delivered by Frank Balbour Browne, Lecturer in Zoology (Entomology) in the University of Cambridge, the subject being "Concerning the Habits of Insects."

Mr. A. O. Trenchan was elected a member.

SCIENTIFIC TEST IN SMOKELESS FUEL PRODUCTION.

The Department of Scientific and Industrial Research has issued an interesting report on the experiment carried out by the Research Board in July, 1924. The test was made on 92 tons of Dalton main coal.

During the test, which those responsible consider was carried out satisfactorily from the technical point of view, samples were taken of the coal and of the products of carbonisation, and the conditions of working and the labour required were carefully oted. The samples collected were all reduced as far as possible and brought to the Research Station for examination. The yields of products per ton of coal carbonized were as follows:—

Coke, 13.92 cwt.
Gas, 5,620 cu. ft., or 39.6 therms.
Tar, 18.62 gallons.
Liquor, 26 gallons.
Crude spirit, 1.78 gallon.
Ammonium sulphate, 13.55 lb.

The coke or smokeless fuel produced was, it is stated in the official summary at the end of the report, of a very suitable size (1in. to 2in. pieces). It was not friable, and contained only 4.6 per cent of breeze. Analysis showed that it contained rather a low percentage of volatile matter (approximately 4 per cent.). When burnt in a household grate it was readily ignited and gave a good hot fire. The fire showed less flame than the coke cakes as manufactured at the Research Station, as was to be expected from its low content of volatile matter.

The *yield* of tar was high, representing 68 per cent. of that obtained *in* the assay apparatus. On examination this tar proved to be a normal low-temperature tar. The yield of gas was fairly high, and throughout the test varied considerably both in volume and in calorific value, owing to variations of pressure in the hydraulic main. The yield of ammonia was also fairly high. The liquor was, however, less than 6oz. strength, and it is questionable whether so dilute a liquor would justify recovery. The spirit obtained by scrubbing the coal gas amounted to 1.78 gallons per ton of coal.

SCIENCE AND LIFE ASSURANCE.

Science enables the great beneficent work of Life Assurance to be conducted on safe and sound lines. One of the most, if not the most, important officials connected with a life office is the actuary, and then there is the doctor, whose work in eliminating bad risks is of far reaching importance. Great Britain is the home and the pioneer of modern Life Assurance. The British Assurance Offices have a world-wide reputation for soundness, for safe management, and for fair dealing in the carrying out of its sacred trust, namely the protection of the family in the time of need.

Some of the offices have latterly branched out in other directions, such as the Wesleyan & General Assurance Society, of Birmingham, which some time ago established a Health Bureau in an effort to still further prolong life, and it is reported that considerable success has rewarded the Society's efforts in this direction. We might mention that while Great Britain can justly claim to be the pioneer of modern Life Assurance, the United States can with equal justice claim to be the pioneer of Health Service in connection with Life Assurance, one large company, the Metropolitan, of New York, having spent vast sums on its Free Health Service during the past ten years; and so successful has this department been, that, owing to the prolongation of the lives of its policyholders, the venture has proved in all respects a financial success—an instance of virtue bringing its own reward.

CHEMISTRY AND WAR.

In the Great War, and especially towards its conclusion, Chemistry played a great part in bringing the world conflict to a triumphant issue. Chemistry is sure to play a predominant part in the next war, let it be soon or late. In connexion with a joint dinner of the Society of Chemical Industry and the Chemistry Industrial Club, at the Hotel Victoria, London, on November 14th, the subject was adverted to by several speakers.

Sir Richard Glazebrook said this country owed its present safety in no small degree to Lord Moulton and those who worked with him in suppying our troops with explosives, and to those chemists who, when called upon, were able to provide protection against the gas attack of the enemy. As to the future, though gas warfare was a hateful crime, he agreed entirely with Professor Smithells that there could be no half-measures of defence, so long as was was possible. It would be dangerous in the highest degree, it would be criminal, if the Army did not put itself in a position to deal with the kind of warfare which the most competent judges of this and other countries believed to be the warfare of the future. To gain security England must appeal to her chemists.

DEPARTMENT OF OVERSEAS TRADE.

Argentine Architectural Design Competition.

The Argentine Government offer prizes of 10,000, 6,000, 4,000, 3,000, and 2,000 Argentine gold pesos for the best architectural designs for a National Institute for the Blind.

Further particulars are available in the Enquiry Room at the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.

COLD LIGHT.

Paris Professor's Research Work.

Professor Risler has been for some time engaged in important research work in connexion with "Cold Light," and there was on view during last week a number of tubes in illustration of the Professor's work, in which he says sought to rival the "glow-worm, which gives light without heat. He claims to have made a tube which yields a 12,000 candle-power light, with an expenditure of 2½ units of electricity. The tube is

filled with atmospheric air at reduced pressure, and are excited by high-ferquency currents. In addition, he employs phosphorescent materials and pigments, either applied to the tubes or incorporated in the glass, to modify the effects. He finds a definite relation between the pressure in the tube and the character of the light emitted, and by suitable adjustments he obtains rays lying between the rose and the violet of the spectrum, without green or red.

After the current has been cut off from them his treated tubes continue to glow, though with diminishing brightness, for a period said to be about equal to that for which they have been excited. Those brought to London are only small—8 mm. in internal diameter and requiring for their excitation a current one-tenth of a milliampere at a pressure of 6,000 volts and of frequency in the neighbourhood of 1,000,000.

DEPARTMENT OF OVERSEAS TRADE.

In view of the probable re-opening of the British Empire Exhibition in 1925, it has been decided to suspend the London Section of the British Industries Fair which would otherwise have been held from the 16th to 27th February. The Birmingham Section of the Fair will, however, be held as usual, and as a special measure for 1925 only, the Birmingham authorities have generously undertaken to organise sections in their Fair for those exhibitors who have hitherto shown in London, provided that the demand for space ensures the adequate representation of the industries concerned. The Department of Overseas Trade expects to resume the series of British Industries Fairs in London in 1926.

FRACTIONAL HORSE-POWER MOTORS.

We touch on this question in another column and are pleased to learn that a list of United Kingdom manufacturers of fractional horse-power motors may be obtained by persons interested on application to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.

MORE WORK FOR BRITISH FIRMS.

The Municipality of Copenhagen have placed another large order for Water Tube Boilers with the Vickers-Spearing Boiler Co., Barrow-in-Furness. This is the second contract the Municipality has placed with this Company recently.

Liquid Chlorine.

It is only within recent years that Liquid Chlorine has been available for commercial purposes, the first plant in this country for the liquefaction of chlorine having been erected by The Castner-Kellner Alkali Co., Ltd., in 1909.

Liquid Chlorine is now delivered in quantity to any part in steel cylinders or tank wagons. It is dry and pure, and does not suffer deterioration in storage, so that it is now used in any convenient place to carry out chlorinations which were impossible a short time ago, when chlorine was available only in the form of its compounds or as a moist impure gas.

The liquid can be handled quite easily without risk, provided the necessary precautions are taken.

Liquid Chlorine boils at -33.6° at 760 mm. It is a dark greenish yellow liquid which solidifies at -102° C. to a yellow crystalline mass.

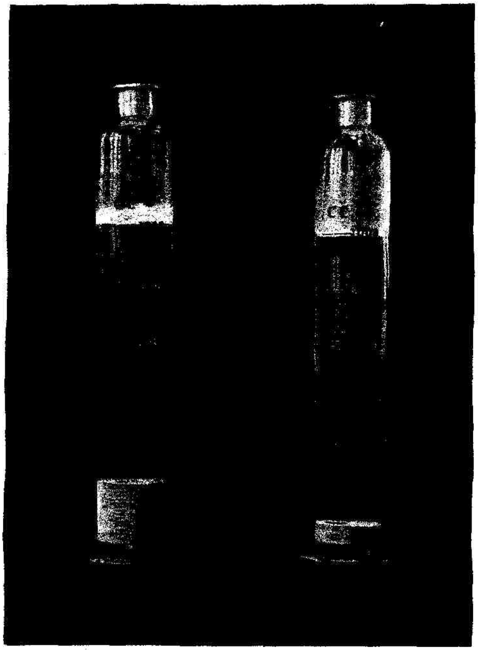
USES OF LIQUID CHLORINE.

The uses of Liquid Chlorine include the preparation of bleach liquor, the production of metallic chlorides, the manufacture of dyestuff intermediates and of non-inflammable solvents, and sterilisation.

Considerable quantities of liquid chlorine are used by bleachers and paper-makers in the preparation of bleach liquor. Bleach liquor is prepared by dissolving bleaching powder in a vat which is provided with an agitator. Calcium hypochlorite, the bleaching agent, is formed in the solution, leaving a sludge which consists essentially of lime mud and occasionally lumps of bleaching powder. This sludge, even after washing, carries away to the dump an appreciable quantity, frequently as much as 10 %, of the available Chlorine.

The recent practice of using liquid chlorine in conjunction with bleaching powder in the preparation of bleach liquors has shown that there is an improved dissolving of the bleach-powder, the lumps are broken down, the lime sludge and the chlorine react to produce more bleaching liquor, and the volume of the sludge remaining is only 25 %, or less, of that obtained by the old method. (Fig. 1.) Moreover, the percentage of available chlorine in this sludge is very much less than that in untreated sludge. In addition, the bleach liquors produced are stronger.

SLUDGE FROM
10° Tw. BLEACH LIQUOR.



UNTREATED. CHLORINATED.
FIG. 1.

Liquid Chlorine is used for the preparation of the chlorides of sulphur, the chlorine derivatives of ethane andi ethylene, carbon *tetrachloride, phosgene, sulphuryl chloride*, aluminium chloride, phosphorus chlorides, silicon tetrachloride, an dthe like.

The *production of intermediates for* dyestuffs requires large quantities of liquid chlorine which is used in the manufacture of benzyl *chloride*, benzyldehyde, benzoic acid, benzoyl chloride, monochlorbenzene, monochloracetic acid, acetic anhydride, *acetyl chloride, tetrachlorphthalic* anhydride, chlorphenols, chlornaphthalenes, and so on. The chlorination of organic sub*stances is also carried out in the manufac*ture of various pharmaceutical products.

In some cases chlorine is used as an oxi*dising agent, e.g., in the production of* potassium permanganate, calcium arsenate, and ferricyanides.

The *detinning of tin scrap is* carried out using chlorine, whereby tin tetrachloride, a liquid which is used for the weighing of silk *fabrics, is produced. Pure tin instead of tin*

scrap may also be used in the manufacture of this substance.

An acid resisting varnish is prepared by the chlorination of rubber.

An aqueous solution of chlorine is the most powerful disinfectant, and the sterilisation of drinking water and waste water by means of liquid chlorine is very important.

See pamphlet, "Chlorine and Chlorine products in relation to public health," issued by Castner-Kelner Alkali Company, Limited.

Recently chlorine has been used successfully in the production of pure cellulose from wood, straw, and various grasses.

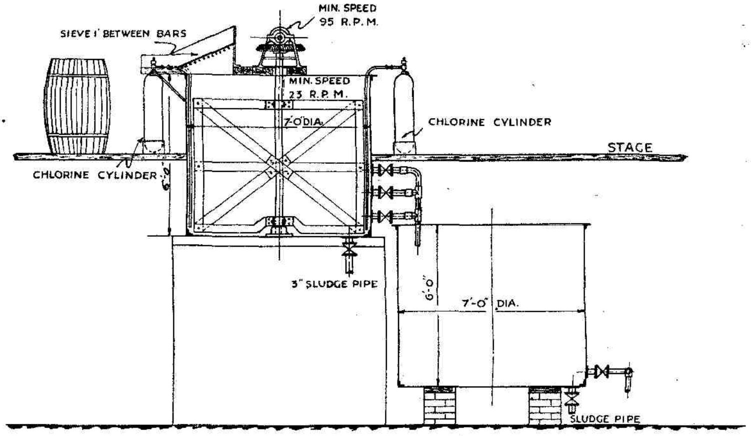


FIG. 2.
DIAGRAM OF BLEACH DISSOLVING PLANT.
Scale $\frac{3}{8}$ in. equals 1 ft.

PROCEEDINGS AND NOTICES OF SOCIETIES.

MINERALOGICAL SOCIETY.

November 4.—Dr. H. H. Thoma, and afterwards Prof. W. W. Watts in the chair.

DR. M. S. KRISHMAN: *Note on Cordierite in a cordierite-gneiss from Madura District, Madras, India.*

Optically positive cordierite occurs in an Archaean gneiss produced by the metamorphism of biotite-gneiss by an intrusive tongue of charnockite. The associated rocks are crystalline limestones (with lime-silicate minerals), and gneisses containing felspars, garnet, sillimanite, biotite, and titanoferrite. Cordierite from two other localities in Peninsular India (Vizagapatam and Travancore) is also known to be optically positive. This positive character is suggested to be due to the isomorphous replacement of MgO by FeO, as in the rhombic pyroxenes, olivines, etc.

DR. A. BRAMMALL: *Lime as a constituent of certain important rock-forming minerals: Its behaviour relative to that of other bases of RO type.*

A review of the facts governing the extent to which RO-bases replace each other in rock-forming minerals, special reference being made to the anti-pathetic relationship between lime and magnesia as constituents of the same simple molecule.

Dr. L. J. Spencer: *An inclusion of magnetite in diamond.*

A minute black fragment (about 1 mg.) taken from a cavity in a diamond from Bultfontein mine, Kimberley, was definitely identified as magnetite. Black inclusions and spots are of common occurrence in diamond, but usually they are non-magnetic and therefore not magnetite.

Dr. L. J. Spencer: *Biographical notices of mineralogists recently deceased (Second series).*

Notices of fifty-five English and foreign mineralogists. The average age of 303 lives (since 1876) is 64 years, and a curve shows a highest point at 74 years. The greatest age was attained by F. E. Neumann (1798-1895), the German crystallographer.

A. Russell: *A notice of the occurrence of native arsenic in Cornwall (with analysis by Dr. H. F. Harward); of bismuthinite at Shap, Westmorland; and of smaltite and niccolite at the Coniston Mine, Lancashire.*

THE FARADAY SOCIETY.

(Continued from Page 328).

A general discussion on "The Physical Chemistry of Igneous Rock Formation," was held jointly with the Geological Society and the Mineralogical Society, on Oct. 22. The following papers were read:—

The Formation of Eutectic end Similar Structures in Silicate Melts, by A. F. Hamilton, M.A., F.G.S.

An account was given of the classification of the silicate salts, the momenclature adopted and the interpretation of the structures.

Proposed Researches on the Chemistry and Physics of Igneous Magmas and Rocks, by J. W. Evans, C.B.E., D.Sc., F.R.S.

The investigation of the origin, history and physical and chemistry characters of igneous magmas and rocks, including in the latter ore bodies believed to be of igneous origin, is of the greatest theoretical and practical importance. On the other hand it is absolutely necessary, if we are to resolve the fundamental problems of the structure and past history of the earth, and on the other it has an immediate bearing on the mode of occurences of metalliferous ores and therefore on the economic problems of mineral production.

There is, however, an important factor that has hitherto not been sufficiently taken into account in studying the genesis both of igneous rocks and of ore bodies. The specimens in our museums and laboratories, however fresh they may be, have not the same composition as the magmas from which they were formed, for these contained a number of constituents of a volatile character that have been since lost, partly as a result of decreased pressure, and partly in the course of the crystallisation of the rock. They comprise hydrogen, sulphur, nitrogen, and other elements, and various compounds, the most important of which are water, carbon monoxide, fluoride of tin and sulphides and arsenides of metals.

On coming in contact with the air in volcanic eruptions the hydrogen, sulphur and carbon monoxide are oxidised with considerable evolution of heat.

Any experiments in which the volatile constituents are not represented by amounts similar to those that are found in natural magmas must be inevitably misleading.

Probably all the reactions and other changes that immediately concern us take place within a depth of 40 kilometres of the surface. Magmas at this depth would be subject to a pressure of some 12,000 kilogrammes to the square centimetre or about the same number of atmospheres, which would be roughly equivalent in British units to 75 tons to the square inch.

If the average downward increase of temperature in the British Isles continued to a depth of 40 kilometres, which however is probably not the cause, the temperature at that depth would be about 1,300° C., but this must be regarded as an excessive estimate. In any case at more moderate depths and in the thick continental shields the temperature must be mnch lower.

The temperature of the crystallisation of intrusive acid igneous rocks and mineral veins does not, there is reason to believe, exceed 750° C., and it must be frequently considerably less. Basic intrusives may crystallise at from 750° to 1,000° C. On the other hand volcanic rocks extruded at the surface may have their temperature raised by oxidation to a maximum of about 1,300° C.

That these pressures and temperatures are

well within the range of experimental investigation is clear from the fact that at the Carnegie Institute pressures up to 20,000 atmospheres and more have been obtained and temperatures up to about 2,500° C. At the same time means have been found of measuring the pressure within 5 atmospheres and the temperature within 2° C.

It is true that the presence of a large proportion of volatile constituents presents additional difficulty, but I understand that this too has been overcome at Washington.

Pressures, however, far higher than those which can be conveniently employed in experimental work must exist in the earth's interior. Calculations from the speed of earthquake vibrations appear to show that a zone of basic silicates simliar in composition to basalt-flows extends downwards from the floor to the zone of acid rocks, which lies normally at a depth not greatly exceeding 10 kilometres below the surface, though in mountain areas it may be as much as 80 or 90 kilometres. At a depth of 1,500 kilometres, where the basic rocks meet, it is believed, on a metallic core, the pressure must amount to well over 200,000 kilogrammes to the square centimetre or 200,000 atmospheres.

Yet the regularity of the rate of increase of the velocity of seismic vibrations both logitudinal and transverse with the depth appears to indicate that the composition of the earth's interior varies but little, and that uniformly, from the base of the acid silicate rocks or magma to that of the basic silicate magma, and that the physical characters of the latter vary uniformly and consistently throughout.

It is therefore probable that any law of variation which holds good in non-mountainous areas for the range of pressure corresponding to depths of from 10 to 40 kilometres may safely be extended by extrapolation to pressures up to that corresponding to a depth of 1,500 kilometres.

THE FARADAY SOCIETY.

The Ordinary Meeting was held on Monday, November 17th, 1924, at 8 p.m., at the Chemical Society, Burlington House, Piccadilly, London, W.1.

Papers were read:—

R. W. E. B. Harman and F. P. Worley: *The Hydrolysis of Alkali Cyanides in Aqueous Solution.*

A. P. Laurie: *Note on the Expansion of Water while Freezing.*

S. S. Joshi: *The Viscosity of Reversible Emulsions.*

D. B. MacLeod: *On the Viscosities of Liquids at their Boiling Points.*

D. B. MacLeod: *The Kinetic Theory of Evaporation.*

J. T. Howarth and F. P. Burt: *New Design for Apparatus to Measure the Coefficient for Acetylene.*

Exhibition of Physico-Chemical Apparatus, by Messrs. A. Gallenkamp & Co., Ltd.

THE INSTITUTION OF ELECTRICAL ENGINEERS.

Savoy Place, Victoria Embankment, W.C.

Wireless Section Meeting.

Wednesday, 3rd December, 1924, at 6 p.m. (Light refreshments at 5.30 p.m.)

"Wireless Telegraph Valve Transmitters employing Rectified Alternating Current," by G. Shearing, Member.

THE CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, December 4th, 1924, at 8 p.m.

The following papers will be read:—

"New halogen derivatives of camphor. Part VI. β-Bromocamphor-α-sulphonic acid," by H. Burgess and T. M. Lowry.

"New halogen derivatives of camphor. Part VII. The constitution of the Reychler series of camphorsulphonic acids. Experiments on chlorosulphoxides," by H. Burgess and T. M. Lowry.

NOTICES OF BOOKS.

Eléments de Chimie Industrielle, par J. Fritsch (Ingenieur-Chimiste.

L'étude de la chimie est à l'ordre du jour. Cette étude s'impose de plus en plus, non seulement aux industriels et aux artisans, mais encore aux contremaîtres et aux ouvriers désireux d'améliorer leur situation morale et matérielle par l'étude et par le travail.

L'ouvrage que nous présentons au public est inspiré de ces considérations. Il a eu un gros succès en Allemagne.

M. Fritsch, bien connu par l'ensemble unique de set ouvrages si appréciés, nous en donne un traductin adaptée au goût francais.

Ce livre est bien fait pour faciliter l'étude

de las chimie; sa clarté et sa concision le mettent à la portée de toutes les intelligences; on le lit sans fatigue tout comme un livre de littérature et on comprend sans effert.

L'ouvrage se divise en trois parties: la premiere comprend l'étude des métalloides, la seconde celle des métaux et la troisième celle des composées de carbone. Il se termine par des notions de thermochimie et d'electrochimie, de décoration des ouvrages métalliques et enfin par l'étude des collar et mastics.

Comme l'indique le titre de l'ouvrage toutes les descriptions qui y figurent sont orientées vers les applications industrielles; il ne contient ni développements spécultatifs ni phrases à effet. C'est la clarté dans la simplicité. Une table analytique soigneusement établie permet de trouver instantanément le mot cherché.

I vol. in 8, Carré 342 pages. Broché, prix 20, frcs. France: France et Colonies 22 frcs. Etranger: 23 frcs. Paris Librairie Genérale Scientifique et Industrielle Desforges, 29, Quai des Grands Augustins.

MESSRS. LONGMAN'S RECENT PUBLICATIONS.

The well-known publishing firm of Longmans, Green & Co., 39, Paternoster Row, London, have recently issued some important works on Chemistry and other scientific subjects details of some of which will be found on the front page of our current issue.

Inorganic and Theoretical Chemistry, by J. W. Mellor, D.Sc., vols. I. to V., £3 3/- per volume, is a comprehensive treatise, which should find a place in the library of everyone interested in Chemistry.

Mathematics for Technical Students, by E. R. Verity, B.Sc., with numerous illustrations, 12/6 net, is a work that ought to appeal to a wide constituency.

Chemistry in the Services of Man, by Alexander Findlay, M.A., F.I.C., 6/- net, is a book that ought to prove very popular.

"ELASTIC GLASS."

Two chemists in Vienna claim to have prepared a synthetic "glass" which possesses the property of not splintering if broken. It is very resistant and elastic. The composition of the substance and the method of preparation have not been divulged, but it appears to be made by some condensation process with formaldehyde.

CORRESPONDENCE.

NOTE ON THE PREPARATION OF THE DI TOLYLTHIOUREAS AND TOLYL ISOTHIOCYANATES.

The Chemical Laboratory,
Highbury New Park, N.5.
November, 1924.

To the Editor of THE CHEMICAL NEWS.

Sir,——In connection with the investigations which are being carried out in this laboratory on the synthesis of the arylamino benzothiazoles, it has becomes necessary to work up relatively large quantities of tolylthioureas and tolyl isothiocyanates.

Di orthotolylthiourea and di paratolylthiourea have been prepared by refluxing the respective toluidines with an excess of carbon disulphide and alcohol, using potassium hydroxide as a catalyst. The crystalline condensation product obtained in this manner being washed with dilute acid, water, spirit, etc., to remove impurities and subsequently crysallised from boiling spirit. The tolyl isothiocyanates have been prepared by the hydrochloric acid hydrolysis of the respective ditolylthioureas in the usual manner.

The thio urea condensations were carried out in the open laboratory using soda lime towers to absorb the worst of the fumes. This has, however, now been found to be a dangerous procedure, for during manipulation of this kind (particularly, say, when 200 gms. of the amine are being converted into the thio urea) most unpleasant and sickening odours are produced; these no doubt are due to either intermediate products or by-products, but even the crystallised thio ureas retain unpleasant odours, and the crude condensation products are particularly unpleasant to handle owing to the physiologcal section of these fumes, which are highly poisonous. It is probable that the poisonous properties of the fumes are partly due to carbon disulphide, which is known to produce fatal results when inhaled in large quantities.

The symptoms of poisoning arising from this work and which I myself have personally experienced are as follows: General heaviness and nausea are first noticed, sickness, salivation, claminess of the skin, sweating, irregular heating of the heart and severe upsetting of the digestive organs follow in succession, convulsions at first mild

and finally violent then set in, these rise to a height, die down, and then repeat themselves in mider form. Dizziness, pains in the heart, coldness of the feet etc., and the usual general symptoms of severe poisoning are also experienced. The general symptoms of a pronounced character last over several hours. The effects are of course apparent for several days after the poisoning (which in my own case was unpleasantly near fatal).

The literature of the subject which has come to my notice does not make any reference to the unpleasant nature of these preparations. In conclusion, I should like to note that a similar but much milder experience was undergone during my work on the preparation of 1 methyl benzothiazole by the direct thionation of acetanilide; distillation of the crude methyl compound obtained in this way yielding a high boiling fraction containing a substance of most unpleasant physiological properties.

Yours etc.,
R. F. HUNTER.

OUR NEATEST AND RICHEST COLONY.

This was the specious description of the Gold Coast (a most unhealthy part of Africa) by Mr. A. G. Kitson, C.M.G., a few weeks back.

Among his chief points were:—The area of the colony is larger than Great Britain; its death rate is lower than our own; its natural wealth is enormous, its reputation for gold dating from 600 B.C.; there are over 400 miles of railway open or nearly completion, as well as about 4,000 miles of motorable roads; a fine harbour is being constructed at Takoradi; cocoa exports have risen from 80 pounds in 1891 to 198,000 tons in 1893; cotton growing is being developed; some 75 per cent. of the world supply of mahogany comes from the Gold Coast; palm oil is an important source of revenue, and fruits of all sorts are abundant.

This Gold Coast might be described as the "white man's grave." A friend, an engineer, who spent some years there, gives us a horrible picture of the climatic and other conditions for the white man. He said the "boys" (meaning the unfortunate natives) die off like flies.

"RAYON."

This is the name suggested for the commodity known as "Artificial Silk," which is proving such a keen competitor to the silk worm.

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

26435—Calder, W. A. S.—Manufacture of sulphuric acid. Nov. 5th.

26215.—Soc. of Chemical Industry in Basle.—Process of making disperse systems. Nov. 3rd.

26628.—Soc. of Chemical Industry in Basle.—Manufacture of esters of unsaturated acids. Nov. 7th.

Specifications Published This Week.

223284—Roucka, E.— Apparatus for indicating or measuring at a distance physical or chemical values.

201912—"Allchemin" Allgemeine Chemische Industrie Akt-Ges, and Jahoda, Dr. R.—Process for the production of phosphorescent zinc sulphide.

223410—British Dyestuffs Corporation, Ltd. Cronshaw, C. J. T., Naunton, W. J. S., and Green, S. J.—Manufacture of diarylguanidines.

215789—Brunner, Mond & Co., Ltd.—Process of making ammonia by catalysis.

Abstract Published This Week.

221592—Fermenting.— Ling, A. R., and Nanji, D. R., University, Edmund Street, Birmingham.

Mashing-processes; wort, producing. — The yield of alcohol obtained by the fermentation of amylaceous mashes or worts prepared with malt is increased by carrying out the preparation or the fermentation of the mash or wort in presence of enzymes which will hydrolize the normally unfermentable β-dextrins and sugars or of organisms which secrete such enzymes. Suitable enzymes are emulsin and the enzymes secreted by organisms of the orders *Aspergillaceæ* and *Penicillium.* The enzymes or organisms may be added with air-dried or green malt in the mashing-process or to the unboiled wort in the fermenting vessel.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

Publisher's Announcements.

The following Books can be obtained from Rea & Inchbould, Merton House, Salisbury Square, London, E.C.4.:

CONFESSIONS OF GREAT SOULS,

By the Rev. J. E. Roscoe, M.A.

This striking work gives extracts (with comments) from the opinions of 50 great writers and thinkers in all ages on Religion. These include Bacon, Balzac, Burns, Carlyle, Cicero, Dante, Darwin, Dickens, Emerson, Faraday, Homer, Huntley, Johnson, Longfellow, Maeterlink, Milton, Napoleon, Newton, Pope, Ruskin, Shakespeare, Socrates, Spenser, Thoreau, Wordsworth, etc., etc.

The work is handsomely bound, and has a copious index for easy reference, and the work, containing as it does the gems of thought on some of the world's greatest thinkers, and will form an acquisition to any library.

By post, 5/- net.

GRAMMAR OF LOGIC.

100 Questions and Answers on The Grammar of Logic or *How to Reason Correctly*, by J. E. Roscoe, M.A., Oxon.

An invaluable book for all who desire to excel as speakers and who wish to reason convincingly.

Post free, 1/7.

BACK NUMBERS AND VOLUMES.

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Various numbers, parts of Vols. 117 and 118 (1918/19) are only on sale at 2s. 6d. each.

THE GENERAL INDEX to VOLS. 1 to 100 can still be purchased at £1 (Carriage Extra).

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THE ORIGINS OF SCIENTIFIC INQUIRY.

By J. G. F. DRUCE, M.Sc. (Lond.), R.Nat.Dr. (Prague).

The steps by which the tremendous volume of scientific knowledge has accumulated will be found most fascinating to trace.

It is now recognised that many hundreds of thousands of years must separate the remotest Stone Age from the earliest communities of which definite historical records exist.

In all stages it will be observed that observations and practical experience came first. Information would accumulate. This would then be co-ordinated and discussed by the more thoughtful of people and finally opinions and theories would be advanced to account for the facts and phenomena of nature.

Man from the earliest times was accumulating the experience and practical skill which are the raw materials in the building up of science. Thus, it has been ascertained that the "Reindeer Men" of the Steppe Periods had implements which could be used for making statuettes and cave pictures. Pottery was probably first made during the Neolithic Age.

The constant repetition, day by day, month by month, or year by year, of similar phenomena must have roused the curiosity of the earliest intellects. Before the dawn of civilisation, the rising and setting of the sun and the moon must have caused men to wonder, especially as their out-door existence favoured such a constant vision of the heavens.

In the day-time the plants and animals with which men came in contact would also command attention and later, inspire interest. It can easily be imagined that in time crops would be raised by the scattering of seeds upon ground prepared in some crude manner.

Since the Babylonians were dependent for their water supply upon the rivers and were surrounded by deserts necessity forced them to study the question of water conservation and irrigation.

By the time that Babylon had reached its zenith, agriculture had developed very considerably and irrigation works had been constructed, thus demonstrating that the Babylonians possessed a certain amount of technical skill.

The Babylonians were pioneers in the making of celestial measurements and observations, although this was closely connected with superstitious ideas. They built temples with towers which served as early observatories, and the earliest record of an eclipse is a Babylonian tablet referring to one which occurred in B.C. 1062. They instituted the seven-day week and used zodiacal signs which were only introduced into Egypt at a much later date. It was the Babylonians, too, who divided the circle into 360 parts or degrees. Besides their astronomical observations, they were able to measure time by means of a water clock. This consisted of two vessels. One was always full of water which flowed continuously into the second, which was weighed. Equal weights of water corresponded with the elapse of equal periods of time.

In Egypt, a shadow-clock was used from very early times. One now in the Berlin Museum bears the name Thothmes III., and therefore dates back to about B.C. 1500.

Technology.—When they carried out the early technical processes of glassmaking, the preparation of soap and the art of dyeing, the Egyptians were following up the work of many earlier generations.

According to Pliny the elder, glass was discovered accidentally by some Phoenician *sailors, who, in the absence of stones, used*

SPECIAL NOTICE.

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lumps of natron (soda) from their cargo to raise their cooking vessels. The heat of the fire melted the natron which then combined with the sand to form a glass.

Metallurgy.—The earliest records of the Egyptians and Indians contain references to the working of different metals. The Egyptians worked the gold mines of Nubia extensively. They were acquainted with gold and silver alloys. Copper, according to E. von Meyer, was first found in the Neolithic stone age. Iron was not discovered until after copper and bronze were known, but the Egyptians were acquainted with the method of tempering steel. Working in bronze dates back to before B.C. 2000. Gold, silver, copper, iron, lead and tin are mentioned in the Old Testament. The general physical attributes of a metal were correctly recognised as glance, ductility and hardness.

Medicine. — The art of administering medicines for the cure of ill-health and disease must have been one of the first branches of science to be practiced. The famous Ebers papyrus, describing early medical methods, dates back, at least, to B.C. 1200. It should be remembered that Egyptian doctors each specialised in one part of the body only. This undoubtedly delayed progress in medical science.

Mathematics.—An important source of information concerning early Egyptian mathematics is the Aahmes papyrus dating back to about B.C. 2000-1700. This manuscript gives directions for attaining " knowledge in all dark things." The mathematics is largely confined to mensuration, geometry being treated superficially. Examples are given of the capacity of barns and the area of certain fields. In calculating, simple fractions $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, and $\frac{2}{3}$ are used as well as whole numbers. The Egyptians had a symbol for two-thirds, but all the other fractions had *one* as the numerator. A kind of algebraic unknown is introduced in the text too. Weights and measures are mentioned and geometrical figures are included. Reference is made to an older writing, now lost, upon the lines of which the Aahmes papyrus was modelled.

All their mathematics was treated from the purely practical standpoint. No attempt was made to examine the subject purely for its own sake. The number 2 was the basis of their calculations, which made these very cumbersome and laborious.

It is interesting to note that they determined the hours of the night by the passing of certain fixed stars over different parts of a watch-keeper's person, whilst he was seated on the ground with a plummet before him.

The planning and execution of the Great Pyramids, too, undoubtedly indicates a high degree of practical skill and an understanding of some mechanics.

It thus becomes apparent that the oldest races with regard to which we possess reliable information, the Egyptians, Phoenicians and Jews, did indeed possess a certain, but very limited, disjointed scientific knowledge which had been acquired accidentally. The earliest cultured European races—the Greeks and Romans—bcame acquainted with some of the more striking scientific phenomena, having obtained their first knowledge of them from the peoples mentioned above. They made no definitely planned experiments of inquiry however, but speculated very freely on the nature of the universe.

THE MOBILITY OF SYMMETRICAL TRIAD SYSTEMS PART II. THE CONDITIONS RELATING TO SYSTEMS TERMINATED BY THE o PHENYLENE GROUP AND DERIVATIVES OF INDENE.

By R. F. Hunter, B.Sc., A.R.C.S., F.C.S., M.S.Chim.

With regard to the discussion of the mobility of systems terminated by phenyl groups, it will be recalled (*The Chemical News*, 1924, CXXVIII., 181) that two classes of evidence were discussed: Firstly (A) Proof that two asymmetrically substituted derivatives which from the methods of their preparation should have formulae such as C_6H_4Ms NH N.N C_6H_5 and C_6H_5NH.N:N.C_6H_4Me, differing only in the position of the mobile hydrogen atom and the double bond are actually identical (symmetry test). Secondly (B) Proof that this single individual behaves as if it were a mixture of the two forms that compose it, by giving four substances instead of two when treated with re-agents that rupture the molecule at the double bond (fission test).

To these a third test was added by Ingold and Piggot (*Jour. Chem. Soc.*, 1923,

CXXIII., 1469) in connection with the second of this series of researches. And it is the intention to discuss in some detail in this connection the investigation of these two investigators on the conditions relating to systems terminated by the o phenylene group and their researches on the indene derivatives (ibid) in the present paper.

The third test to which reference has been made above is (C) Proof that the single individual referred to in (A) behaves as if it were a mixture of the two forms by giving two isomeric compounds such as C_6H_4Me NR N:N C_{65} and $C_6H_5NR.N:N.C_{64}Me$. when the mobile hydrogen atom is replaced by an alkyl group or acyl group and which may be termed the substitution test. These three tests of mobility have been shown to invariably support one another in the expected manner.

In Part I it will be recalled that the four systems

.N(H).N:N. .N(H).CH:N. .C(H).N:C: and :C(H).CH:C:

were studied as regards their mobility when terminated by two phenyl groups, and the conclusion was drawn that whereas diazoaminobenzene (I) and diphenylformanidine (II) are undoubtably tautomeric, the systems present in benzylidenebenzylamine (III) and diphenylpropene (IV) are quite devoid of mobility, so much so that isomeric change could not be observed even at relatively high temperatures.

(1) $C_6H_5NH.N:N.C_6H_5$

$C_6H_5.CH$ .N:CH C_6H_5 (III)

(II) $C_6H_5NH.$ CH:N. C_6H_5

C_6H_5CH CH : CH C_6H_5 (IV)

These facts having been established, it was decided by Ingold and his collaborators to turn next to the corresponding series of cyclic structures in which the two phenyl groups of the first series are replaced by a single phenylene group. The four parent substances therefore being aziminobenzene, benziminazole, isoindole and indene.

With regards the first of these cyclic systems, Griess at an early date drew the conclusion that aziminobenzene is symmetrically constituted because two aziminobenzoic acids, which form their mode of synthesis, should have formulae differing in the presence of the carboxyl group in the fused homocyclic ring were found to be identical (*Berichte* 1882, XV., 1878), a result which was later confirmed by Zincke and Helmert (*Annalen*, 1896, CCLXXXXI., 313). Aziminobenzene satisfies what has been termed by Ingold, the symmetry test (A) and although no suitable way of applying the fission test (B) has been found, it is interesting to note that the substitution test (C) is satisfied. Zincke and Lawson (*Annalen*, 1887, CCXXXX, 119) by acetylation of aziminotoluene obtained a mixture of two isomeric acetyl derivatives which on hydrolysis gave back the same aziminotoluene. Zincke and Lawson themselves regarded the acetyl compounds as physical isomerides, but this they are certainly not, for they can co exist in solution both at high temperatures and at the ordinary temperature. There can be no question but that they are structural isomerides, and the fact that on hydrolysis they give the same aziminotoluene constitutes additional evidence of the mobility of the three nitrogen system present in the compound.

The same two types of evidence (A and C) support each other in proving the mobility of the triad system in benziminazole. Thus the rational synthesis of 2:6 dimethyl and the 2:5 dimethyl derivatives (numbering from the NH of the heterocyclic ring in a clockwise direction) leads actually to a single individual which, on methylation, gives a mixture of two isomeric N methyl derivatives which are then 1:3:6 and 1:3:5 trimethyl derivatives (*Jour. pr. Chem.* 1906, (ii) LXXIII., 419, 1907 (ii), LXXV., 88).

Up to this stage the parallelism with the open chain series in which the triad system is terminated by two phenyl groups, holds good, both in the open chain and in the cyclic series the systems NH.N:N and NH.CH:N are actively tautomeric. Therefore, it is clear that particular interest attaches to the two remaining types, namely the isoindole and indene types containing the systems CH.N:C and CH.CH:C which are known to be inactive when terminated by phenyl groups. It is unfortunate in this connection, however, that it has not yet been possible to complete the intended comparison, for although indene is the parent of a large and important series of compounds for which several methods of preparation are known, neither isoindole nor any of its

derivatives appears to have been hitherto prepared, and in this connection it is obvious that it is not only necessary to synthesise isoindole itself and study its reactions, especially the fission and substitution reactions, but also to work out general methods of preparation of derivatives suitable for the application of the various tests for mobility already discussed; Ingold and his collaborators were therefore compelled to undertake a somewhat lengthy investigation on the chemistry of isoindole and its derivatives before making an attack on the special problem of the tautomeric mobility of the compound, and it appeared desirable in the meantime therefore to push forward the projected series of experiments on the tautomeric mobility of indene. The results of the research of Ingold and Piggot justified this decision, for their experiments yielded the first evidence of a marked difference between the structural conditions present in the open chain and cyclic series. Unlike diphenylpropene, which is definitely static, indene is mobile, being strictly comparable in this respect with aziminobenzene and benziminazole.

It is not necessary to discuss in detail the previous investigations which have been made to examine the mobility of indene by the symmetry method, because these attempts have invariably involved substitution in the three carbon system itself. Thus it will be recalled in this connection that Courtot (*Compt. rend.* 1915, CLX., 523) showed that 1 benzylindene prepared from benzyl chloride and magnesio indene is different from, but readily convertible into 3 benzylindene, which Thiele and Buhner had previously prepared from benzylideneindene by reduction. (*Annalen*, 1906, CCCXLVII., 249). No attempt was made by Courtot to detect the reversibility of the *interconversion* which he had observed, and whether or no the benzylindenes are actually the individuals of a tautomeric system cannot be deduced from Courtot's work. But even if they are not, it would not follow that the unsubstituted three carbon system present in indene itself is not mobile, because it has been shown by Bland and Thorpe (*Jour. Chem. Soc.* 1912, CI., 871 and 1740) that the presence of an alpha or gamma benzyl group suppresses the mobility of the three carbon sytem of glutaconic acid to a remarkable extent.

It is, however, clearly unnecessary to tamper in any way with the three carbon system of indene to obtain experimental proof or disproof of its symmetry. One can proceed as follows: first two substituted indanes, one a 1:5 derivative and the other a 1:6 derivative, are synthesised, and each of them rigorously orientated; then by elimination of the group H.X each indane is converted into an indene which is substituted only in the benzene nucleus, the *identity or non identity of the monosubstituted* indenes so obtained and establishes the symmetry or dissymmetry of the unsubstituted triad system present in the indene system. This is the plan on which the work of Ingold and Piggot was based and the results of their experiments clearly demonstrate the symmetry of the indene system. The experiments throughout were directed to the production of a pair of isomeric 1 hydrindamines, either of the 1:5 and 1:6 types or the 1:4 and 1:8 types from which ammonia could be eliminated to give substituted indenes. With this in view, a close study was made of a considerable number of indanes in which the substituent group in the benzene ring was NO_2, NH_2, NHAc, OH, or Me, whilst the other group was either NH_2 or some group which could readily be converted into an amino group.

Kipping and Revis had shown (*Jour. Chem. Soc.* 1897, LXXI., 250) that 1 hydrindamine itself can readily be prepared by the reduction of the oxime of 1 hydrindone, which in turn can be prepared by the action of aluminium chloride on the chloride of β phenylpropionic acid. The general plan was therefore to carry out a similar series of preparations starting with o, m and p substitution products of β phenylpropionic acid. It will, however, be observed that whilst o and p substituted phenylpropionic acids can give rise respectively to 4 *and 6 substituted* hydrindones and hydrindamines only, m substituted phenylpropionic acids on the other hand might give rise to 5 and 7 derivatives of indane. For this reason and also because this method as a source of indanes is further greatly limited by the fact that the chlorides of substituted phenylpropionic acids do not always undergo internal condensation in the presence of aluminium chloride as readily as does β phenylpropionyl chloride itself, it became necessary at an early stage in the investigation to discover a means of supplementing existing synthetical processes by finding some new sources of substituted 1 hydrind-

amines. The direct introduction of substituents into 1 hydrinamine itself and into 1 hydrindone appeared to offer possible methods of preparing the required isomeric hydrindamines, and a preliminary investigation was therefore undertaken by Ingold and Piggot with a view to the preparation of substituted hydrindamines and hydrindones directly from the parent substance. The tracing out of the inter relationship and the orientation of the series proved a tedious task, but it was finally completed and resulted in the synthesis of a pair of isomerides of the type required.

It is well-known that aniline on nitration in concentrated sulphuric acid yields the meta substitution product, whilst acetanilide under similar conditions gives the para compound. Therefore, one of the first plans adopted consisted in directly nitrating 1 hydrindamine and its acetyl derivative, for if there were any difference between the directive influence of the amino sulphonic and acetylamino groups, these reactions would lead to two nitrohydrindamines having the required relationship to each other. It was found, however, that the nitration product of acetylhydrindamine, shown to be the acetyl derivative of 6 nitro 1 hydrindamine was identical with the acetyl derivative of the nitration product of 1 hydrindamine itself. The two nitro compounds yielded on reduction the corresponding amino compounds on the identification of which the orientation of this series of 6 substituted 1 hydrindamines depends.

The second starting point was 1 hydrindone, the nitration of which was attempted by Kipping, who obtained, under conditions which he himself found difficult to reproduce, a very impure product containing however a crystalline nitrohydrindone. This substance when pure melted at 76° to 77°, but it was obtained only in small quantities and was difficult to purify (*Jour. Chem. Soc.* 1894, LXV., 495) so that no attempt was made to determine the position of the nitro group or to characterise the substance by the preparation of derivatives. More recently (*Berichte* 1916, IL., 1279), von Braunt and Heider carried out the same nitration but did not try to purify the product.

The nitration of 1 hydrindone was carefully examined by Ingold and Piggot, who evolved a process by means of which it is possible to obtain a quantitative yield of a mixture of two mono-nitrohydrindones which owing to their extraordinary tendency to crystallise from solvents, may be separated from one another and obtained in a pure condition. The two compounds melt at 74° and 77° and it is probable that the higher melting compound is the one which was isolated by Kipping.

The orientation of these two substances practically resolves itself into deciding whether they are 6 or 4 nitrohydrindones and this is accomplished by oxidation. It is well known that 1 hydrindone on oxidation with cold alkaline permanganate gives phthalic acid. If, however, dilute chromic acid is employed homophthalic acid may be isolated as the main product. Exactly similar results were obtained using the nitro hydrindone melting at 74°. Cold alkaline permanganate converted the compound into 4 nitrophthalic acid and dilute chromic gave 4 nitrohomophthalic acid as the main product of oxidation, whose constitution follows from the fact that it is nearly the sole nitration product of homophthalic acid itself, and on further oxidation it gives 4 nitrophthalic acid. This relationship between the nitro ketone and the two nitro acids was further confirmed in two ways. In the first place the nitro ketone was converted into its oximino derivative by treatment with amyl nitrite and hydrochloric acid, the oximino compound hydrolysed by hydrochloric acid and formaldehyde to the corresponding 1:2 diketone and this on oxidation with dilute chromic acid passed smoothly into 4 nitrohomophthalic acid. The second method consisted in first converting the nitro compound into its 2:2 dibromo derivative and then oxidising this with permanganate to 4 nitrophthalic acid. The nitro hydridone melting at 74° is then clearly 6 nitro 1 hydrindone (V).

$$NO_2C_6H_3 < \begin{matrix} CH_2 \\ CO \end{matrix} > CH_2 \text{ (V)}$$

6 Nitrohydrindone having been thus orientated, it became possible by establishing a connecting link with the nitration products obtained from hydrindamine and acetylhydrindamine to orientate these substances. The nitro ketone (V) or its dibromo derivative was first reduced by stannous chloride to the amino ketone which was then acetylated and the acetyl derivative converted into the oxime. This gave

on reduction an acetyl derivative of hydrindamine which on further acetylation gave a diacetyl componnd identical with the product of acetylation of the compounds derived by the reduction of the nitration products of both hydrindamine and acetylhydrindamine, these substances are therefore clearly 1:6 disubstituted indanes.

The second isomeric nitrohydrindone melting at 77° proved on examination to be a remarkably stable molecular compound of 6 nitro hydrindone and 4 nitrohydrindone. Not only was it incapable of being resolved into the simple ketones by fractional crystallisation, either from solvents or from the molten substance, but it also yielded a single oxime and semicarbazone, from both of which it could be regenerated; whilst fractional oxime and semicarbazone formation had no effect on its melting point or crystallographic homogeneity. On bromination, however, it yielded a mixture of 2:2 dibromo 6 nitro hydrindone and the isomeric 2:2 dibromo 4 nitrohydrindone, the structure of which is indicated by its oxidation by permanganate to 3 nitrophthalic acid. Similarly on reduction the higher melting nitro ketone yields a mixture of 6 aminohydrindone and 4 aminohydrindone, the latter can also be obtained by the reduction of the dibromonitro compound and its orientation follows from this fact.

Whilst these experiments were in progress *on the production of 1:4 and 1:6* disubstituted indanes, a second series of experiments were commenced with the object of working out methods for the preparation of isomeric 1:5 and 1:7 derivatives. After a number of unsuccessful experiments, a satisfactory starting point was found in m methoxy β phenylpropionic acid, which can be synthesised from m nitrocinnamic acid by reducing this with stannous chloride, diazotising the tin double salt of the base, decomposing the product with boiling water, methylating with methyl sulphate the phenolic acid so obtained and then reducing the unsaturated methoxy acid to the corresponding saturated acid.

$$NO_2C_6H_4\ CH:CH\ CO_2H \rightarrow NH_2C_6H_4CH:CH\ CO_2H \rightarrow$$
$$OH\ C_6H_4\ CH:CH\ CO_2H \rightarrow OMe.C_6H_4\ CH:CH\ CO_2H \rightarrow$$
$$OMe\ C_6H_4CH_2CH_2COOH \rightarrow OMe\ C_6H_4CH_2CH_2COCl$$

It is clear that the chloride of this acid might rise either to 5 methoxy or 7 methoxy 1 hydrindone when internally condensed by means of aluminium chloride. Actually the condensation was found to give an excellent yield of a single methoxy ketone together with a phenolic by-product consisting of two isomeric substances which were readily identified as 5 hydroxy 1 hydrindone and 7 hydroxy 1 hydrindone, both of which had been previously described by Auwers and Hilliger (*Berichte* 1916, IL., 2410). The methoxy ketone was identified as 5 methoxy 1 hydrindone by preparing it from 5 hydroxy 1 hydrindone by methylation with methyl sulphate in alkaline solution. Further, the methoxy ketone on oxidation by means of chromic acid yields a methoxy homophthalic acid together with 4 methoxyphthalic acid.

It became clear at this point that while the first series of experiments starting from hydrindamine and hydrindone was leading to 1:6 derivatives, the 1:4 isomerides being produced only in small quantities, the second series starting with nitrocinnamic acid was leading mainly to 1:5 disubstituted indanes and only to a small extent to 1:7 isomerides. This at once settled the question as to the orientation of the isomeric hydrindamines which were to be synthesised for conversion into the possibly identical indenes, and it was decided to employ the information which had been gained regard*ing the synthetic methods available for the* preparation of the 1:5 and 1:6 disubstituted indanes. The starting points selected were th representative in each series which had been namely 5 methoxy 1 hydrindone and 6 amino 1 hydrindone.

The conversion of 5 methoxy 1 hydrindone into 5 methoxy 1 hydrindamine (VI) was readily accomplished by reducing the oxime with sodium amalgam and acetic acid. 6 Amino 1 hydrindon was converted into 6 methoxy 1 hydrindamine in the following steps: The 6 amino ketone was first diazotised under conditions carefully adjusted so as to avoid the introduction of an oximino group in the position 2, and the 6 hydroxy 1 hydrindone thus obtained methylated with methyl sulphate. The methoxy ketone was then converted into the methoxy ketoxime which on reduction yielded 6 methoxy 1 hydrindamine.

$$MeO\ C_6H_3 < \begin{matrix} CH\ NH_2 \\ CH_2 \end{matrix} > CH_2$$

(VI)

$$MeO\ C_6H_3 < \begin{matrix} CH_2 \\ CH \end{matrix} > CH$$

(VII)

The two methoxyhydrindamines as well as the methoxy ketoximes, the methoxy ketones and the hydroxy ketones of the 5 and 6 substituted series were found to be different from one another. Nevertheless, the two methoxyhydrindamines when converted into their salts, readily lost ammonia yielding the same methoxyindene (VII).

The formation of the indene takes place with remarkable ease. Thus the hydrochlorides of the two hydrindamines, on melting in the absence of any reagent, give an immediate precipitate of ammonium chloride from which the indene can be removed by filtration or distillation. It was characterised by Ingold and Piggot by the formation of a crystalline picrate and crystalline dibromide.

It is clear from this that the triad system in indene satisfies what has been termed the symmetry test (A) for mobility. There remained to apply the tests (B) and (C).

Firstly it was anticipated that in the fission test (B) that indene on oxidation would give a mixture of 5 methoxy and 4 methoxy homophthalic acid along with 4 methoxyphthalic acid. The experiment, however, proved difficult and although it was found possible to obtain a partly crystalline oxidation product by the use of cold dilute chromic acid, only two of the three acids mentioned were isolable in a pure condition, the acids isolated being 5 methoxyhomophthalic acid and 4 methoxyphthalic acid.

With regards the third test (C), namely the substitution test, this yielded interesting results. One of the simplest means of replacing the potentially mobile hydrogen atoms in indene appeared to be to condense it with benzaldehyde which it was expected would give rise to a mixture of two benzylideneindenes, or possibly the hydrobenzyl derivatives of these substances (*Annalen*, 1906, CCCXXXXVII., 268). Actually a mixtures of two compounds corresponding in composition with the aforesaid hydroxybenzyl compounds were islated, but it was not found possible to isolate them in a pure condition.

From these investigations it will be seen that the three carbon system in the indene nucleus is a mobile system, and since it [illegible] of substitution and probably of fission also, it must be regarded as in every way comparable with the mobile systems present in benziminazole and aziminobenzene, the evidence provided by the work of Ingold and Piggot being strictly parallel to that supplied by Fischer in one case and by Griess and Zincke in the other.

Highbury New Park.
N.5.

October, 1924.

General Notes.

TRADE WITH CANADA.

Industry Gets Foot-and-Mouth Disease!

The Federation of British Industries have again demonstrated their great ability to promote the best interests of British trade in connection with the recent regulations of the Canadian Government respecting the importation into Canada of all foods packed in straw or such-like materials.

The question arises out of an order issued by the Dominion Government in August last providing that owing to the outbreak of foot and mouth disease in his country, all packing consisting of straw and such-like materials sent with goods arriving in Canada must be *accompanied by a certificate signed by a "veterinary officer of the Government."*

Complaints were at once made to the Federation of trades interested, particularly the Pottery trade, of their difficulties in complying with this order. The Pottery Federation had installed a large and expensive disinfecting plant in order to comply with similar legislation previously brought in by the U.S.A. and in complying as best it could with the new Canadian legislation, had supplied its members with straw from this plant and advised them to send with each consignment of goods a certificate supplied by a veterinary surgeon. But this was not enough for the Dominion authorities, who pointed out that it was essential for all certificates to be signed by a *veterinary officer of the Government.*

The F.B.I. then took up the question with the British Ministry of Agriculture and at the same time with the Dominion Ministry of Agriculture. The latter, realising the difficulty caused to British manufacturers,

agreed that shipments containing such packing despatched prior to the 15th November should be admitted if accompanied by an ordinary certificate signed by a veterinary surgeon.

At the same time the British Ministry of Agriculture informed the Federation that they had themselves informed the Canadian Ministry of Agriculture that no veterinary officers were maintained by the Ministry in this country, available for the signing of such certificates, on receipt of which information the F.B.I. suggested to the Canadian Government that they might see their way to accept certificates signed by ordinary veterinary surgeons.

This suggestion was met with a refusal on the part of the Canadian Government to *depart from the provisions of the original* regulation making the signature of a Government veterinary official necessary. From the 15th November, therefore, *a complete stoppage of consignments of British goods into Canada packed in straw or similar packing was in prospect.*

The situation was one of great gravity, realising which the Federation took up the matter once again with the Ministry of Agriculture that it is now satisfactory to be able to announce that, in response to the representions made the Ministry of Agriculture have agreed to nominate veterinary surgeons in required areas as representing the Ministry, who shall be empowered to issue certificates in accordance with the requirements of the Canadian Government.

STAINLESS STEEL.

At an informal meeting on Friday, November 21st, of the Junior Institution of Engineers, Mr. J. C. Hopcraft spoke on the subject of "Stainless Steel." He dealt with the methods of working the metal by forging, casting and rolling etc., and with *heat treatment. He said that it should be* understood that the special properties of stainless steel were inherent properties and not merely superficial. The properties of withstanding heat and corrosion and remaining bright were produced immediately after tempering and removal of the scale, with polishing if necessary. The fact that the steel had to be heat-treated after being worked imposed a limitation on the size of job which could be undertaken, so that the production of large girders, for instance, was not a commercial proposition at the present time. Stainless steel had good heat-resisting qualities and would not scale up to about 800 deg. C., the effect on the surface being confined to colour effect only. Another trouble encountered at present was the removal of scale from the inside of long tubes and similar inaccessible positions. Stainless steel could not be expected to machine like mild steel, but with the right degree of hardness and a little experience in the use of the tools for the particular job, the turning and screwing etc. of the metal could be carried out without much difficulty. A new stainless steel combining a high degree of resistance to corrosion with extreme malleability had recently been brought out under the name of "Stabrite." This metal could be produced in sheets for cold-pressed articles which required no further heat treatment. It could not be hardened, but could be welded, soldered, and brazed fairly easily. Mr. Hopcraft said that the earlier failures of some stainless cutlery were invariably due to wrong heat treatment or wrong forging. Unnecessary allowances were made at first for wear due to polishing knives in machines, a process absent with stainless steel, but now a properly forged blade could be sharpened by any means and be entirely satisfactory.

SCIENCE AND THE SMOKE NUISANCE.

Before the Royal Institute of British Architects on 19th November, Professor Julius Berens Cohen delivered an address on Smoke, its cause, nature, effects, and methods of prevention. He said that soot from factory chimneys was very different in character from that from domestic fireplaces, where raw coal was burnt. In the former case, owing to the high temperature and strong draught, the volatile portions of the coal were mainly consumed, while the draught carried off mechanically fine mineral dust and grit mixed with carbon containing little tar. Domestic soot, on the other hand, might contain as much as a quarter of its weight of tar. It was this tar which caused the soot to cling, accumulating with time, and blackening every surface it touched with a varnish which was not re-

moved by rain. Vegetation suffered in several ways from the presence of smoke, for the normal growth of plants depended on light falling on the green surface of the leaf. Again, the plant was affected by the acid soot, and also from the sulphur acids which passed into the air from burning coal, and were washed down by rain. The effect of this acid was to corrode the leaf, which withered and fell much earlier in and near a town than in the country. Moreover, the acid percolating through the soil destroyed certain organisms and enzymes concerned in the assimilation of the soil constituents, and many grasses, vegetables, and flowering plants succumb. Even the colour of flowers was affected. Historic and beautiful buildings all over the country were undergoing slow but certain destruction. Fabrics, leather bindings, and metal-work were being similarly attacked.

What was the remedy? So far as factory smoke was concerned, the Public Health Act of 1875 gave powers to the local authorities to stop unnecessary smoke, and ample evidence was forthcoming before the Committee on Smoke Abatement that boiler chimneys need not smoke. A strict enforcement of these powers would stop the great bulk of factory smoke. It was difficult to legislate for the domestic fireplace. Gas and electricity were coming more and more into prominence for cooking and heating, and that was a good sign. A good deal more might be done by the gas undertakings to promote the consumption of their coke. They had their show places for gas-cookers and gas-fires. Why not other show places for coke stoves (of which there were many on the market), where they could be seen at work, and where the cost of installation and maintenance could be ascertained? Cheaper gas, cheaper coke, cheaper electricity, and an energetic local authority encouraging their sale, while holding a firm hand on the offending boiler chimney, would clear the air of most of the smoke.

WILL THE UNIVERSE DISAPPEAR?

Mr. G. F. Foxwell writes to the London *Times*:—

Dr. Jeans's paper, so ably summarized by Dr. Turner, leads to an interesting inquiry. Assuming without question the correctness of the theory that light and heat are material, it follows that all stars and other hot bodies are losing mass. Conversely, bodies absorbing heat are gaining mass; but, taking the universe as a whole, only a very small fraction of the mass lost by hot bodies is gained by cooler bodies. Hence, in the course of ages the universe as we know it will disappear. If space is infinite our universe will vanish into radiations which travel on for ever. We are thus left with the fundamental difficulty of explaining how matter came into being. Will these radiations by any known process enter into the formation of another universe?

ANCIENT SUN WORSHIPPERS OF PERU.

On November 27th, at King's College, London, the London Consul General for Peru, Senor Salomon, delivered an interesting lecture on Ancient Peru. He pointed out that the ruins of the Inca civilisation were spread over a wide area from Panama to Chile, embracing Columbia, Ecuador, Peru, and Boliva. But still more important than the Inca civilization was the fact of a pre-Inca civilization, called Tia Huanco, superior to that of the Inca, the remains of which—monuments, monoliths, palaces, fortresses, &c.—were found scattered over Boliva, in Cuzco, round Lake Titicaca, and in many other places. The proper name of this pre-Inca civilization was Tahuantisuyu, which meant a country divided into four districts—north, south, east, and west.

As for the Incas, they were a great agricultural people, and the remains of their canals and aqueducts, which modern engineers considered as serviceable as those constructed to-day, might be seen in many places, especially along the coasts of Peru. The Incas worked the metals—gold and silver. While failing to attach value to them like the moderns, they ornamented their palaces, temples, and fortresses with them, and the specimens in the British Museum of their gold and silver works were proofs of their artistic ability.

They had no rich, and no poor. But (said the lecturer) everyone was happy and discontent was unknown among them. The State did everything for its subjects, interfering in all things, even in the affairs of private life. Indeed, the system was Socialistic. There were three classes—the

Royal Family, the priests, and the people. The Chief Priest and the Head of the Army were drawn from the Royal House. The Inca had many wives and a large progeny, and he married his sister in order to keep the Royal blood unmixed. Every man of 21 and every girl of 18 was compelled to marry. To every child born a piece of land was given—a boy getting more than a girl. All the work was done by the people, and every person—man, woman, and child (from five upward)—had his or her allotted share of work to do. No one was permitted to be overworked, but no one dare be lazy under penalty of death as a punishment for such a crime against the State. The agricultural season was opened by the Inca himself with a golden plough. It was very curious to note that in the remoter parts of Peru to-day many of those old customs were still followed, and the old communistic spirit still prevailed. Transport was on the backs of the natives or by the llama—the camel of Peru for immemorial ages.

SURGICAL BOOTS.

"The Lancet" of November 22nd contains an interesting illustrated article on this subject, by Charles MacKay, M.D., and D. Denham Pennock, F.R.C.S.Eng. The article seeks to formulate some definite principles to be followed in the ordering of Surgical Boots. It says:—

The ordering of surgical boots is not infrequently *considered* by the general practitioner to be the exclusive privilege of the orthopædic surgeon or of the so-called surgical bootmaker. This abdication of one of the realms of treatment is unnecessary in many cases, and in the latter instance may result in much harm to the patient. Practitioners risk the loss of both prestige and patient by sending a case of foot deformity to a surgical bootmaker for treatment. To us this is a confession of weakness. We consider that every practitioner should be able to order an ordinary surgical boot with knowledge of the therapeutic requirements, and of the effect likely to be produced.

There are many essential practical details *of the actual making of a surgical boot* which must necessarily be left to the skill and experience of the surgical bootmaker. The type of boot, however, should always be prescribed by the medical attendant, and whenever possible with the bootmaker present. We have come into close contact with many surgical bootmakers, and it is rare in our experience to find one who could be depended upon to supply a completely satisfactory surgical boot on his own initiative. The practice of patients going indiscriminately to surgical bootmakers is one to be strongly condemned. The majority of conscientious bootmakers would, we consider, greatly prefer a surgical prescription into which they could put all the skill and knowledge at their command. To be able to order surgical boots satisfactorily presupposes some orthopædic knowledge, but it is a comparatively simple matter, and in its main principles is not difficult to comprehend.

PLATINUM AND ALLIED METALS.

(DEPARTMENT OF THE INTERIOR, WASHINGTON).

By James M. Hill.

PRODUCTION.

CRUDE PLATINUM.

Mine returns for 1923 indicate a production of 7 troy ounces of crude placer platinum in Alaska, 578 ounces in California, and 24 ounces in Oregon, a total of 609 ounces for the United States. In 1922 Alaska produced 39 ounces, California 916 ounces, and Oregon 53 ounces.

Platinum refiners report purchases of *domestic platinum in 1923 as follows:* Alaska, 29 ounces; California, 707 ounces; Oregon, 63 ounces; Washington, 1 ounce—a total of 800 ounces, which is 258 ounces less than was purchased by refiners in 1922. Refiners also report purchases of 54,741 ounces of foreign crude platinum in 1923, including 1,007 ounces from Australia, 10 ounces from Canada, 48,727 ounces from Columbia, and 4,997 ounces from Russia. As reported by the Bureau of Foreign and Domestic Commerce, Department of Commerce, the imports of platinum from Columbia during 1923 were 32,278 ounces, and the total imports of unmanufactured platinum 86,417 ounces, a decrease of 9 per cent., as compared with imports in 1922.

REFINED PLATINUM METALS. NEW METALS.

Reports of refiners of crude platinum, gold

bullion, nickel, and copper indicate that 49,797 ounces of platinum metals were recovered from these sources in 1923, a decrease of 7,921 ounces as compared with the recoveries in 1922. It is estimated that of the total quantity, 3,472 ounces was derived from domestic sources.

Platinum in Different Centres.

	1922	1923
	oz.	oz.
California	916	578

The 1923 results were obtained from 48,190,740 yards of gravel. In 1921, from 400 yards of gravel 208 ozs. of osmirulium were saved on Yodda and Gira Rivers Papua.

Canada 1922.—National nickels of Canada produced 176.18 oz. of platinum, 341.44 oz. of palladium, and 124.44 oz. of rhodium, ruthenium, osmium and irridum.

Columbia—In 1922 40,000, and in 1924 43 oz. of crude platinum were produced.

South America—15,259 oz. platium in 1922, and for 8 months of 1923 7,697 oz. *were produced by the S. American Gold and* Platinum Co.

Russia.—In 1922, 22,000 oz. of platinum and in 1923 60.5 poods, equal to 31,362 oz. of platinum, were recovered.

[Pood is a Russian measure of weight.]

GOLD, SILVER, COPPER, LEAD, AND ZINC IN THE EASTERN U.S.A. STATES.

Mine Production.

The total value of the gold, silver, copper, lead, and zinc mined in the Eastern States in 1923 showed an increase of about 13.7 per cent. from the corresponding value in 1922. Of the total value gold represented $11,919; silver, $89,215; copper, $3,011,-647; lead, $175,000; and zinc, $14,765,885. The increase was caused mainly by the increased output and the higher selling price of copper, lead, and zinc.

The principal feature of mining in these States in 1923 was the extended operations of the large companies that produce copper and zinc and the lessened activity at the small gold placer and deep mines.

BITUMINOUS SANDS OF NORTHERN ALBERTA.

The High Commissioner for Canada in London has received from the Dominion Department of Mines at Ottawa a small stock of the report by Mr. Sydney C. Ells on the Bituminous Sands of Northern Alberta, containing a general description of the area underlain by bituminous sands; general desreiption of the deposit; particulars of sampling and laboratory determinations and of commercial applications, etc. Copies of the report may be obtained on application either to the Department of Mines at Ottawa or to the Office of the High Commissioner for Canada, Kinnaird House, Pall Mall East, S.W.1.

DRUGS, AND MISCELLANEOUS STORES, ETC. FOR EGYPT.

The Ministry of the Interior, Egypt, is calling for tenders to be presented in Cairo by noon on the 6th January, 1925, for the supply of drugs, dressings, glassware, brushware, etc. required for the drug stores of the Department of Public Health for the period of one year from April 1st, 1925, to March 31st, 1925.

The conditions of tender, specifications, etc., may be inspected by firms interested in the supply of British goods at the Department of Overseas Trade (Room 53), 35, Old Queen Street, London, S.W.1.

THE BRITISH METAL CORPORATION LIMITED.

Captain Oliver Lyttelton, D.S.O., has been elected to a seat on the Board of The British Metal Corporation, Ltd., and has been appointed a joint Managing Director.

PROCEEDINGS AND NOTICES OF SOCIETIES.

ROYAL SOCIETY.

262nd Anniversary Meeting.

The 262nd Anniversary Meeting was held on December 1st, at Burlington House, London, Sir Charles Sherrington, the President, in the chair, announced that a third Yarrow Professorship had been provided from the munificent gift of their Fellow, Sir Alfred Yarrow, to which Professor Richardson, noted for his work on the emis-

sion of electrons from hot bodies, had been appointed.

The Society's medals were awards as follows:—

The Copley Medal to Sir Edward Sharpey Schafer, for his researches in physiology and microscopical anatomy.

The Rumford Medal to Mr. Charles Vernon Boys, for his services to physical science by producing apparatus for accurate physical measurements and by making measurements of a high order of accuracy.

A Royal Medal to Sir Dugald Clerk, for scientific work largely as the result of which the internal combustion engine is taking the place of steam-power in smaller ships and workshops as a prime mover of moderate power, and to-day that engine renders possible the motor-car, the aeroplane, and the submarine.

A Royal Medal to Dr. Henry Hallett Dale, for researches to the action of Ergot by which a fresh key has been furnished both for study of the normal circulation and also for the problem of baffling pathological condition.

The Davy Medal to Professor Arthur George Perkin, for researches on the natural organic colouring matters and other natural products, notably the colouring matter of cotton flowers.

The Darwin Medal to Professor Thomas Hunt Morgan, for his researches into the theory of organic evolution.

The President devoted his Presidential Address to the researches in nerve-physiology, in which for 15 years Professor Magnus and his collaborators have been engaged in the Utrecht laboratory, and have now brought to approximate completion. Its field, he said, had lain in nervous mechanisms which, though the highest part of the brain could have touch with them, could yet of themselves work wholly reflexly and separately from mind. A number of simpler acts, studied for the most part in lowlier animal forms, had, of course, long been known to stand in that relation to the higher brain. But the Utrecht researches proved a like relation, and in the superior mammals, for acts surprisingly complex, the assumption and maintenance of the erect posture of walking, running, and so forth in all their ordinary completeness. Not only had Magnus and his colleagues observed this, but they had analysed the reflex processes by which these acts were thus accomplished. They had traced the seat and nature of the stimuli at work, the principles of the co-ordination of the nervous arcs and muscles involved, and, indeed, all the mutual interaction which grade and secure the nicety of adjustment exhibited in such complexity.

Plant-growth orientated itself in regard to the line of gravity, geotropism; and so in the rabbit, cat, and monkey, standing, walking, running with their element in common, the erect attitude, were shown by Magnus and de Kleyn to be, shortly said, refined geotropic reflexes. Any position other than the erect one excited in the reflex animal restoration of its erectness. The head, for instance, is righted by an act having its unconscious source in the pull and pressure of two microscopic stones in the special pair of tiny gravity organs bedded in the skull. With righting of the head goes rotation of the eyeballs in the opposite sense, keeping the vertical meridan of each retina in correspondence with the actual vertical. Appropriate reflexesc brought the whole animal from any other position into the symmetrical right-side-up one. The well-known manœuvre which enabled the cat, when inverted and falling from a short height, to right itself in the air during its fall, alighting squarely on its feet, was shown by Magnus and his colleagues to be executed perfectly by reflex action, after removal of the entire higher brain. Detailed analysis proves this whole reaction to be a chain of reflexes again essentially geotropic.

"Following these researches," the President continued, "we see, therefore, that it is less true to say the higher animal under direction of its mind keeps itself right side up than to say that the animal body by automatic mechanism is kept right side up. From the animal's point of view, as a sentient being, for it to be right side up to the world is, of course, for the world to be right side up to it. In other words, the body's automerism ensures that the mind, looking, so to say, out from the body, finds the world right side up. By the Utrecht researches that relation is shown to be maintained by processes as non-mental as is digestive secretion of the bile. Hence, this right-side-upness geing settled without mind, and indeed prior to mind, and naive mind being, whatever else it is, utilitarian, the situation has not invited consideration from naive mind.

"Mind has not needed, so to say, to think about a relation already existent and given it from the outset. Professor Magnus's researches enable us, therefore, to trace how, in the make-up of mind, right-side-upness of the world comes as an innate unargued datum, an immediate intuition, there being no direct sense-experience of its origin or *elemental processes, although confusion in* mental space when its elements conflict. William James, with characteristic picturesqueness, wrote that our 'pre-historic ancestors discovered the common-sense concepts,' among them what he termed 'one-space.' With that we may set 'world right-side-upness'; but as for dating its 'discovery' to our prehistoric ancestors, it, as an immediate intuition, must date back not to the merely prehistoric, but to the entirely prehuman."

The following officers and members of council were elected: — President, Sir Charles Sherrington, Treasurer, Sir David Prain; Secretaries, Mr. W. B. Hardy and Mr. J. H. Jeans; Foreign Secretary, Sir Richard Glazebrook; other members of Council, Sir Frederick Andrewes, Professor J. H. Ashworth, Dr. F. W. Aston, Sir William Bragg, Professor S. Chapman, Sir Dugald Clerk, Dr. H. H. Dale, Professor F. G. Donnan, Professor A. S. Eddington, Professor E. S. Goodrich, Sir Thomas Holland, Professor J. B. Leathes, Professor T. R. Merton, Dr. G. C. Simpson, Professor J. F. Thorpe, and Professor F. E. Weiss.

THE JUNIOR INSTITUTION OF ENGINEERS.

Friday, 5th December, at 39, Victoria Street, at 7.30 p.m.—Lecturette, "Metal Cutting Under Water by the Oxy-acetylene Blow Pipe," by J. B. Polland (Slides and demonstrations).

Friday, 12th December, at 39, Victoria Street, at 7.30 p.m.—Ordinary Meeting. Paper, "Fluid Transmission Gears," by H. G. Bouly *(Associate Member), (Slides).*

THE FARADAY SOCIETY.

"Base Exchange in Soils."

A group of papers on this subject will be presented for discussion at a meeting of the Faraday Society to be held in the rooms of the Chemical Society, Burlington House, London, on Tuesday, December 9th, at 4.30 to 7.30 p.m.

The chair will be taken by Sir Daniel Hall, Scientific Advisor to the Ministry of Agriculture, and an Introductory Address will be given by Dr. D. J. Hissink, of Groningen.

Further particulars may be obtained from the Secretary of the Faraday Society, 90, Great Russell Street, London. W.C.1.

Programme.

Professor N. M. Comber (University of Leeds): "The Role of the Electronegative Ions in the Reaction between Soils and Electrolytes."

H. J. Page and W. Williams (Rothamsted Experimental Station): "Studies on Base Exchange in Rothamsted Soils."

Professor G. W. Robinson and Rice Williams (University College, Bangor): "Base Exchange in Relation to Soil Acidity."

S. J. Saint (University of Leeds): "The Relation between the pH Value, the Lime Requirement and the Thiocyanate Colour of Soils."

E. A. Fisher (Research Association of British Flour-Millers): "Some Secondary Aspects of Base Exchange in Soils."

INSTITUTION OF PETROLEUM

Eighty-First General Meeting.

At the House of The Royal Society of Arts, John Street, Adelphi, W.C.2.

On Tuesday, 2nd December, 1924, the following Papers were read—

"Fuel Oil Resources of the Future," by A. W. Nash, B.Sc., M.I.Mech.E., and H. G. Shatwell, B.Sc. (Vict.), M.S. (Tech.), A.I.C.

"The Somerset Oil Shales," by H. G. Shatwell, B.Sc. (Vict.), M.S. (Tech.), A.I.C., A. W. Nash, B.Sc., M.I. Mech.E., and J. Ivon Graham, M.A., M.A., M.Sc., A.I.C.

THE CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, November 20th, 1924, at 8 p.m.

The following papers were read:—

"The Sulphur Compounds of Kimmeridge Shale Oil. Part I." By F. Challenger, J. R. A. Jinks and J. Haslam.

"The interaction of thiocyanogen and of hydrogen sulphide with unsaturated compounds. Part II." By F. Challenger and T. H Bott.

THE INSTITUTE OF PHYSICS.

The following have been elected to Corporate Membership:—

Fellows.—L. F. Bates, J. H. Field, H G. Hughes.

Associates.—D. Gunnaiya, A. Subrahmaniam.

ROYAL MICROSCOPICAL SOCIETY.

The Section of the Society which has been formed to deal with the Industrial Applications of the Microscope, and to assist in the development of Scientific Research in British Industries, held its meeting at 20, Hanover Square, W.1., on Wednesday, 26th November, 1924, at 7 for 7.30 p.m. It was a Joint Meeting with the Institution of Structural Engineers. Mr. Percy M. Stewart (Chairman of the Amalgamated Portland Cement Manufacturers) presided.

Mr. Joseph E. Barnard, F.R.S., F.Inst.P., F.R.M.S., gave the second Lecture Demonstration on "The Elementary Principles of Microscopical Illumination:—(2) Self-Luminous Objects."

Mr. H. J. Deane, M.Inst.C.E., M.Inst. M.E. (Vice-President of the Institution of Structural Engineers) "The Application of Microscopy to Cement Research."

Exhibits were shown before and after the meeting by Messrs. Chapman & Alldridge, Ltd. Metallurgical Microscopes with Dark-Ground Illuminating Objectives for examining Opaque Minerals.

NOTICES OF BOOKS.

A History of Bleaching, by S. H. Higgins, M.Sc., with nine illustrations. Pp. viii. + 176. London: Longmans, Green & Co. Price 10/6 net.

The author is obviously au fait with both the theory and practice of his subject. He traces the history of bleaching in early times, referring to the account of dyeing and washing in Pompeii by Sir William Gell. The fullonica, where the washing was carried on, consisted of a white marble building, with fountains and cisterns for washing and dyeing one of the plates shews how the process was carried on in these early times. The account is of considerable interest to all connected with the dyeing and kindred industries. Chapter II. deals with the seventeenth century period, two illustrations shewing the method of finishing in Ireland in the eighteenth century. It would seem that forgery of trademarks was very prevalent at this time, and although the art of bleaching in Ireland, England and Scotland was in an embryonic stage, so much so that for a time most of the bleaching was done in Holland. The various stages of the improvement in the art of bleaching the various chemical inventions and the Pioneers of the Industry are dealt with in a sympathetic and clear manner, while at the end of the work are given tables shewing the actual cost of bleaching and the materials used in the process in the eighteenth century. The printing is clear and the binding strong and appriate, and the work will be a useful addition to any chemical library.

Practical Organic Chemistry, by Julius B. Cohen, Ph.D., B.Sc., F.R. Pp. 520. London: MacMillan & Co. 6/6.

The present is the third edition of the above work which is an evidence of its popularity. There is a copious alphabetic index, numerous illustrations, and the book is divided into various sections. Section III. is composed of notes on the biochemical preparations. Near the end of the book are given tables shewing the melting-points and boiling-points of groups of organic compounds and their derivatives.

Constituents of Coal Tar, by Percy Edwin Spielman. Pp. 220. London: Longmans, Green & Co. 12/6 net.

This is one of the popular monographs on Industrial Chemistry, Edited by Sir Edward Thorpe, C.B., LL.D., F.R.S., and it certainly is not one of the least interesting of the long series already published by Messrs. Longmans, Green & Company. The Bibliography at the end of the book considerably enhances its value. There are given two folding charts and there can be no doubt about the object of the book being fulfilled,

namely, " to be of interest to those chemists who are interested in the Individual Constituent substances that together form Coal Tar."

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

27129—Anjow, K.—Treating tungsten ore to obtain tungsten oxide. Nov. 13th.

Specifications Published This Week.

201555—Chemical Treatment Co.—Process of desulphurizing iron, steel ,erro-alloys, and other metals and composition of matter for use therein.

215705—Dextrin Automat Ges—Process for the liquefaction and saccharification of starch.

202629—Gaillard, E. A.—Manufacture of sulphuric acid.

224065—Coignard, A. J.—Process for obtaining a deposition of chromium by electrolysis.

210465—Soc. of Chemical Industry in Basle.—Manufacture of thionapbthisatin and its intermediate products.

213571—Kassner, Dr. G.—Catalytic oxidation of ammonia.

Abstract Published This Week.

222159—Calcium salts; adsorbents for liquids and gases.—Sauber, J. N. A., 43, Johanna-Verhulststraat. Amsterdam, Holland.

Calcium carbonate, sulphite, sulphate, phosphate, tartrate, and oxalate; gases separating mixtures of; liquids, purifying; purifying saccharine liquids; oils, purifying —Calcium salts having adsorbent properties suitable for the treatment of liquid such as sugar solutions or oils and of gases and vapours are prepared by converting calcium oxide or hydroxide into an insoluble salt by treatment with an acid in presence of an alkali metal hydroxide or salt or with a large excess of an alkali salt with subsequent treatment of the solution remaining by an acid to regenerate the alkali salts. The calcium salts mentioned are the carbonate, sulphite, sulphate, phosphate, oxalate and tartrate, the particular description relating to the production of carbonate. Milk of lime mixed with a solution of potassium or sodium carbonate or hydrate is treated with carbon dioxide at 90° C. or higher. The precipitate may be washed with various liquids; for instance, for use in the treatment of oils it may be washed with soda solution, benzine or alcohol, and the precipitate may be used wet or wholly or partially dried; and various substances may be admixed with it such as amylum, gelatine, casein, tannin, or soda which prevent the particles from adhering to each other and facilitate their contact with the liquid to be treated. Alternatively finely divided lime or milk of lime, together with caustic alkali or alkali carbonate is distributed in a chamber into which carbon dioxide is admitted together with steam or superheated steam preferably under pressure; calcium sulphite may be made by employing sulphur dioxide and sufficient superheated steam. Alternatively a large excess of sodium carbonate is added to milk of lime, an excess of 25 or 50 per cent. being suitable; and before or after the separation of the precipitate the solution is treated with carbon dioxide or flue gases to conver the caustic soda formed into carbonate for re-use.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

PUPIL ASSISTANT. A Vacancy will shortly occur in the Laboratory of a London Public Analyst.—Apply, Young, 24, Aldgate, London, E.1.

NORTHERN POLYTECHNIC INSTITUTE.

HOLLOWAY, LONDON, N.7.

The Governors of the above Institute invite applications for the post of full-time teacher (male) of Chemistry, involving its application to the Building and the Rubber trades. Salary—London County Council scale. Candidates must be Graduates of an University, preferably with Honours Degrees.

Particulars and forms of application to be obtained from the Secretary.

Publisher's Announcements.

The following Books can be obtained from Rea & Inchbould, Merton House, Salisbury Square, London, E.C.4.:

CONFESSIONS OF GREAT SOULS,

By the Rev. J. E. Roscoe, M.A.

This striking work gives extracts (with comments) from the opinions of 50 great writers and thinkers in all ages on Religion. These include Bacon, Balzac, Burns, Carlyle, Cicero, Dante, Darwin, Dickens, Emerson, Faraday, Homer, Huntley, Johnson, Longfellow, Maeterlink, Milton, Napoleon, Newton, Pope, Ruskin, Shakespeare, Socrates, Spenser, Thoreau, Wordsworth, etc., etc.

The work is handsomely bound, and has a copious index for easy reference, and the work, containing as it does the gems of thought on some of the world's greatest thinkers, and will form an acquisition to any library.

By post, 5/- net.

GRAMMAR OF LOGIC.

100 Questions and Answers on The Grammar of Logic or *How to Reason Correctly*, by J. E. Roscoe, M.A., Oxon.

An invaluable book for all who desire to excel as speakers and who wish to reason convincingly.

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CHEMICAL NEWS, MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

EARLY GREEK SCIENCE.

By J. G. F. DRUCE, M.Sc. (Lond.), R.Nat.Dr. (Prague).

Whilst the first faint suggestions of science appeared in Babylonia and Egypt, it was in Greece that science first began to take definite shape.

The military successes of the Greeks during the fifth century B.C. and consequently the firmer establishment of the nation led to commercial success, and as wealth increased so more leisure was obtained for the pursuit of Art, Philosophy and Science.

Alongside the development of the drama, sculpture and architecture, the knowledge of science increased too.

EARLY GREEK SCIENCE.

Thales of Miletus (about B.C. 640) was the first Greek philosopher who can claim any attention for his work in science. His discoveries in astronomy and his knowledge of that subject were used for the advantage of the Greek sailors. The accurate prediction of an eclipse in the sixth century, B.C., and the discovery of certain mathematical laws are attributed to him, and for these he received the title of one of the " seven wise men " of Greece.

He regarded water as the source of all matter. His crude speculations concerning the origin and nature of the universe were of necessity premature, and were no more than guesses. They were gradually superseded as more exact knowledge began to be acquired.

In accordance with the custom of his time, Thales regarded the earth as flat and floating upon water. He succeeded, however, in marking out the solstices and equinoxes and determined that there were four seasons to the year and not two as had previously been supposed.

Anaximander (about B.C. 610), a contemporary and friend of Thales, is credited with the invention of the sun-dial so that time could be told from the position of a shadow cast by a pin upon a metal plate. He also worked out the moon's phases, showing he knew that the moon travelled round the earth.

Another Ionian Greek, Anaximenes about B.C. 580-530) studied the heavens, which he considered to move as a whole whilst the earth was stationary. Unlike his compatriots he regarded air, not water, as the source of all things. Earthquakes, according to him, were caused by the breaking up of hills.

One of the most celebrated early Greek scientists was Pythagoras, who was born at Samos about B.C. 582. During his youth, he came in contact with Thales and also visited Egypt, where he perfected his knowledge of geometry. He founded a school of philosophical and mathematical thought, which accomplished much in the way of learning. His teaching formed the bulk of the mathematical knowledge down to the Middle Ages and included the rudiments of solid geometry.

The Egyptians already knew that if a triangle be constructed having its sides 3, 4, and 5 units long, the angle opposite the longer side is a right angle. This fact they made good use of in building.

Pythagoras probed the problem until he had solved it and the theorem enunciating this still goes by his name. The solution of this problem opened up new possibilities in mathematical deductions, and Euclid's first book is practically devoted to the proof of this theorem. Pythagoras also worked out a number of other propositions which were afterwards incorporated in the first two books of Euclid. Indeed, many of the propositions in the first, second, fourth and sixth books of Euclid were worked out by him and his pupils.

Later, Pythagoras went to Babylon and further East before returning to his home, where he taught such as would come to him.

LATER GREEK SCIENCE.

Towards the close of the fifth century, B.C., Athens became the centre of learning. The philosopher Anaxagoras introduced the new idea of the " Mind " which he stated reduced " Matter " to an orderly system.

The first scientific inquiries into medicine and pharmacy were made by Hippocrates of Cos (about B.C. 460), a pupil of Democritus. A rudimentary knowledge of anatomy was obtained and Hippocrates was able to predict the natural cause which certain diseases followed. He regarded air, water, and environment as the three deciding factors which normally affect the health.

This was a period of much speculation on the part of the Greek philosophers. Little of their work is of any scientific interest, but reference may be made to those philosophers who also contributed to the development of mathematics and science generally.

Plato B.C. 427-347), the friend and follower of Socrates, was one of these. He materially developed Greek thought, including a knowledge of mathematical science.

Whilst primarily a philosopher, Plato set a high value on the study of arithmetic, the measurement of length, surface and depth, and on a study of the revolution of the stars. Such studies, he asserted, had an elevating effect upon the mind of the student.

Up to his time, Greek mathematics was mainly the work of the Pythagorean School. It was Plato who roused a wider interest in the subject.

A contemporary of his was Archytas (about B.C. 428-347) who worked out a number of geometrical problems and applied his knowledge of mathematics to the advancement of mechanics.

Many distinguished mathematicians lived during the fourth century B.C., and among them Eudoxus (about B.C. 406-355) was probably the greatest. Eudoxus came in contact with both Plato and Archytas and became not only a mathematician but also an astronomer of note and a physician. In mathematics he increased the number of theorems and studied proportions. In astronomy he explained how the planets moved round the heavens and calculated the times of their re-appearance. At this time Democritus also suggested that the " Milky Way " was made up of millions of stars, scattered like dust in the sky.

The spherical shape of the earth had been asserted by Parmenides, who was the first to regard the moon's light as reflected light, but his work was not characterised by definite proofs.

That the earth was a sphere, was not generally accepted by the Greek philosophers. Plato assumed it was at the centre of the universe and therefore it did not require any support. By a combination of arithmetical and geometrical progressions he endeavoured to estimate the relative distances of the Moon, Sun and Venus and other planets from the earth.

The earth's rotation upon its own axis was first taught by Heraclides in the fourth century B.C. He is also credited with the opinion that the morning and evening star (Venus) revolves around the sun.

About B.C. 400 the Athenian, Meton, found that nineteen years corresponded closely with 235 lunar months and for this he proposed 125 months of 30 days and the remainder to have 29 days. Each years thus contained 365¼ days.

The Atomists.—The versatile Empedocles (about B.C. 450) was another man who can claim attention as contributing to the advancement of science. He is credited with the enunciation that the universe may be analysed into four elements, which were characterised by their properties apparent to the touch:—

Earth	...	Cold and dry.
Air	...	Hot and moist.
Fire	...	Hot and dry.
Water	...	Cold and moist.

This idea was developed by a group of Greek philosophers, including Aristotle, and was taught and believed as complete for many centuries to follow.

According to the theory in its complete form, matter was regarded as compounded from the foregoing properties.

It was suggested by Democritus (about B.C. 460-370) that matter could be repeatedly sub-divided until the ultimate particles or atoms were reached. All changes of matter were regarded by him as due to the various separations and re-combinations of the atoms which were considered to be in continual motion.

The Atomists, as these philosophers came to be called, accounted for the differences observed in various kinds of matter as being due to the properties inherent in matter. This led to the conviction that one kind of matter can be transformed into another. The belief that water could be converted into air was natural, as both had the common property of dampness, and coldness—the other property of water, can be changed by the addition of heat, thus rendering the product damp and hot, *i.e.*, having the properties of air. They assigned to the particles of the earth a cubic shape, to those of the air an octahedral shape, while those of fire were considered tetrahedral and those of water icosahedral.

From the above-mentioned doctrine of the elements, the idea of the Transmutation of the metals arose.

In order to meet certain difficulties in this theory of the Atomists, Aristotle introduced the idea of the existence of a fifth element οὐσία, which in recent times has been regarded as possibly corresponding with the ether.

Contemporaneous with the Atomists were the Sophists, who were a class of private lecturers who instructed young men who had completed an elementary education. The Sophists came into prominence owing to the power acquired by the Athenian popular assemblies. They taught chiefly rhetoric and oratory, but incidentally a little knowledge of mathematics and astronomy was disseminated by their aid. This professional class lived upon its teaching and many Sophists became rich, but they did not achieve any real advance in scientific thought.

There lived at this time the greatest of all Greek philosophers, Aristotle (B.C. 384-322), who was chosen by Philip of Macedon as the tutor of his son who became later Alexander the Great. Aristotle therefore had at his disposal almost unlimited means and was able to organise scientific inquiries on an extensive scale. For instance, for his work on Natural History, Alexander arranged for him to employ several thousands of men to collect specimens and information over a wide area in both Europe and Asia.

Aristotle enumerated the different sciences, arithmetic, geometry, astronomy, the study of motion, harmony and logic. His scheme of knowledge was more comprehensive than anything before.

He has been called the founder of Zoology since he began a classification of animals from an examination of the different parts of their bodies. He traced the development and gradual differentiation from the lowest animal to the highest and noted that the differences between the lowest plants and the lowest animals were slight. He incidentally pointed out that plant life was a lower form of life than that possessed by animals.

Aristotle's contributions to astronomy include the belief that the stars, like the earth, are spherical, but in this branch of knowledge he was more a compiler than an original worker. His observations were mediocre and his deductions frequently wrong, but he certainly advanced science, especially by his spirit of inquiry into the secrets of nature.

Among the pupils of Aristotle was Theophrastus (about B.C. 371-286), who made a study of plants. He observed that some produced flowers whereas others did not. He described over 500 species, chiefly of medicinal value, dividing them into trees, herbs and shrubs. His writings are of especial value for their criticism of the empirical knowledge of the times.

Just at the close of the era of Greek Science came Euclid, the compiler rather than the discoverer. In his writings he co-ordinated the knowledge accumulated by others.

It may be noted how Greek science, after concentration at Athens, flourished rather on the periphery of the Hellenic world than at the centre.

Discoveries in science were now being made by Greek scholars at Alexandria. The work of Euclid and later Greek scientists and mathematicians must be included in the advances once against achieved in Egypt.

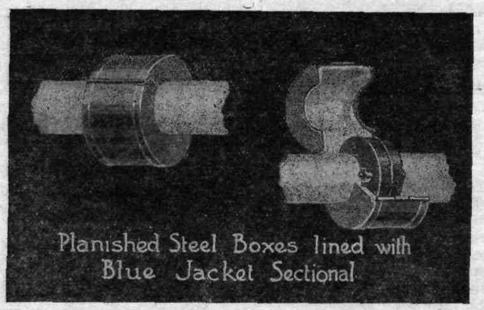
BLUE ASBESTOS.

A Valuable Material for Chemical Works.

In the chemical industries the value of ordinary white asbestos (chrysotile) does not require much emphasis, whether for the resisting of acids or the non-conductivity of heat. It is not generally realised, however, that the somewhat rare variety of asbestos known as crocidolite or blue asbestos possesses far superior properties in both these connections.

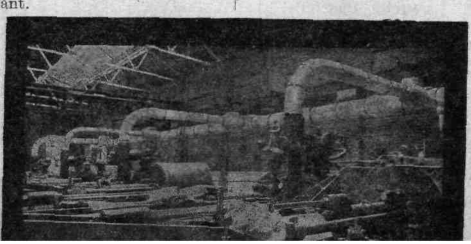
Blue asbestos is a natural and complex silicate which differs from the ordinary white

variety in containing a considerably high percentage of iron, which accounts for the deep lavender blue colour, whilst also the magnesia and combined moisture content are lower. It is found in South Africa, having been discovered and its use subsequently developed in many different fields by the Cape Asbestos Co., Ltd., of London, who own their own mines in Griquland (South Africa) the material being treated at the Company's works at Barking (London). As compared with white asbestos, the fibres are longer, average ¾″ to 2″, and have a considerably higher tensile strength, whilst it is much lighter in weight, a point of considerable importance in many directions, for example, in reducing the load carried by a long steam pipe circuit. It is not only the best practical non-conductor of heat known, being 20% better than white asbestos, as shown by the tests at the National Physical Laboratory, saving up to 93-94% of the heat radiated from a bare steam pipe, but it possesses also the very great practical advantage that it does not deteriorate and lose its fibrous conditions under the highest temperatures, even up to 800° F. (425° C.) so that it can be used direct on the pipes in modern superpower station work without the complicated proceeding of using special compositions to take the first shock of the heat. Incidentally it may be mentioned that even under the blowpipe flame it only loses about 5% by weight.



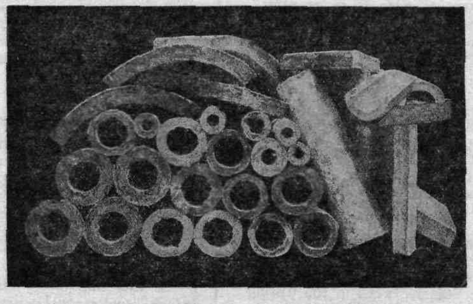
For steam pipes the material is supplied generally in the form of moulded segments of any desired diameter, split in the centre so that they are easily attached, whilst also the rope, plaited, or mattress form can also be used as required, not only for pipes and boilers but also stills, evaporaters, and other chemical plant.

The material is also easily applied to steam pipe xanges either in the form of a special mattress with hooks, or better by means of special metal flange boxes, containing either flat moulded segments or the loose product.



Its properties in the way of acid resisting are even more striking. Thus even with concentrated nitric acid between the temperatures of 16°-110° C. the loss in weight varies from zero to 4½%, whereas good white asbestos is 11% up to 62%, whilst in the case of hydrochloric acid blue asbestos loses about 3½% at 16° C., rising to 10% at 110° C., and the average white asbestos figure is 13½ loss at 16° C., rising to 64½% at 110° C., somewhat the same results obtaining for other acids, such as sulphuric.

As a result, blue asbestos constitutes the highest grade material for such uses as basin rings for the concentration of sulphuric acid, in the manufacture of acid proof cements mixed with silicate of soda, for packing nitric acid towers and acid pumps, as a strong net which does not become brittle for the platinum catalyst in the manufacture of oleum, and for completely acid proof filter cloth, supplied in standard 25 yard rolls either 40″ or 48″ wide.



General Notes.

LIVINGSTONE COLLEGE, LEYTON, LONDON.

We have to acknowledge the Annual Report of the above, which was incorporated in 1900. During that time we learn that 810 have entered for the full course or part of it.

SUGAR BEET.

An effort has been made with indifferent success to manufacture Sugar Beet in Great Britain. In order to stimulate the Industry and enable the manufacturers to make it a commercial success it is proposed to give a Government subsidy for a period of ten years, subject to certain simple conditions, easy to be complied with. For one thing, not less than 75 per cent. of any machinery and plant to be used in any factory for the manufacture of Beet Sug must be British. It will also be a conditio of payment of the subsidy that the sug manufacturers should pay during the fir four years a minimum price of 44s. per to of beet of 15½ per cent. sugar content, wi an addition or deduction of 3d. per ton respect of each one-tenth per cent. of sug content above or below 15½ per cent.

The proposed subsidy, which will app to sugar manufactured during the curre season, will be at the rate of 19s. 6d. p cwt. for the four years from 1924-25 1927-28 inclusive; at the rate of 13s. p cwt. for the three following years; and the rate of 6s. 6d. per cwt. for the thr final years. These rates will apply to sug of a polarization exceeding 98 deg.; sugar of lower polarizations the rates w be reduced according to scale. The subsi has been fixed at a rate which will enab the sugar factories to pay excise duty at t preferential rate, which at present is 8 2-3d. per cwt., and the industry would be adversely affected in future by any red tion in the Customs duty on imported sug

since the Excise duty would be proportionately reduced at the same time.

SCIENCE AND HOUSE BUILDING.

Science is at last taking an active and definite interest in the well-discussed subject of Building. The Building Research Board (Department of Scientific and Industrial Research) is investigating the question in its various aspects. Dr. R. E. Stradling, the Director of the above Board, states that "Some of the foremost scientists in this country are now at work. There is, for example, the committee that investigates the structure of building. Under modern conditions of heavy road transport, and therefore of increased vibration, the problems of the loading and strength of such buildings need scientific investigation. The chairman of the committee is Professor C. F. Jenkin, who is Professor of Engineering Science at Oxford. Other members are Dr. Stanton, of the National Physical Laboratory, one of the most experienced engineering scientists in the country. Professor A. Robertson, from Bristol University, who did extensive work in the testing of timbers during the war, and Professor A. J. S. Pippard, of Cardiff, a specialist on the analysis of stresses in structure.

"This team of scientists are already applying their experience to meet certain exceptional difficulties in the building industry, an industry in which science has never played a large part, and which mainly works on certain somewhat vague rules handed down from past generations.

"Another problem of house construction is called technically 'weathering.' It is of fundamental importance in house building that the materials used should resist the wearing effects of time and weather, but unfortunately comparatively little is known by modern science about this factor in building construction. New materials are produced by inventors, and without extensive laboratory tests it is sometimes difficult to state with any degree of accuracy whether houses built of the new materials will be satisfactory in respect of 'weather.' In order to assist on the chemical and geological aspects of this problem, among others, a second committee of five scientists, four of whom are Fellows of the Royal Society, has been appointed by the Government. The chairman is Sir H. Jackson, formerly Professor of Chemistry in the University of London. The members are Professor C. H. Desch, Professor of Metallurgy at Sheffield University, Dr. A. Scott, the Director of the Research Laboratory at the British Museum, Mr. J. A. Howe, of the Geological Survey, and Professor J. W. McBain, Professor of Physical Chemistry at Bristol.

"With the assistance of these scientists endeavours are being made to discover the effects upon materials used in building of amount of moisture in the atmosphere. It changes in the temperature and of the is a surprising fact that certain materials, as, for example, Yorkshire sandstone, 'breathes' due to a variation in moisture content, *i.e.*, changes in volume with change in moisture accompanied by large changes in strength. The work already started under the Stone Preservation Committee, especially concerned with the decay of stone work, is fully reported on in the annual report of the Department."

ROYAL SOCIETY'S ANNIVERSARY DINNER.

At the Anniversary Dinner, at the Hotel Cicil, London, on December 1st, over which the President Sir Charles Sherrington presided, the Secretary of State for the Colonies, Mr. L. S. Amery, in proposing "The Royal Society," said that but for science the British Empire could never have held together. What submarine telegraphy had done in the best, new means of communication were doing every day from the point of view of the personal contact and communication which alone could keep the independent members of our Commonwealth united in action. Every development of science that facilitated rapid and speedy intercourse was of immense importance. The time might come when the statesmen of the Empire might be able to converse with each other over the long-distance telephone. Again, the developments of the airship and the aeroplane might make it possible for those Conferences of Empire, which to-day were assembled with such difficulty and such real embarrassment to many of those concerned once every two years or so, to be called together at far more frequent intervals.

It was on scientific development, more than on any constitutional scheming, that the future unity of the Empire in large

measure depended, and getting in touch with or of going to other regions of the Empire. The development of the Empire was going to depend, in no small degree, upon making it habitable for its people. There was the field of research into health, and primarily into health in tropical countries, in which their society had done and could do a wonderful work.

They were only at the beginning of that work. There was an immense field to be covered before the tropical regions of the world, the most fertile and most productive, could be made really healthy for their own population and also—and this opened up a very wide vista—for populations of the white race.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE ROYAL SOCIETY.

Nov. 13th. Papers read:—

SIR ARTHUR SCHUSTER, FOR. SEC. R.S.: *On the Total Reflexion of Light.*

N. K. ADAM and J. W. W. DYER: *The Molecular Structure of Thin Films. Part VI.* Communicated by W. B. Hardy, Sec. R.S.

(1) Five long-chain alcohols have been examined by previously described methods. The area of cross-section of the chain in the alcohols is the same as in the acids, within 2½ per cent., and the CH_2OH group occupies 21.6 sq. A.U. of area.

(2) The acetates of these alcohols pack with the heads occupying 23 sq. A.U., and form expanded films of the same kind as other esters.

(3) The methyl ethers of the alcohols do not form stable films, the methyl group destroying the anchorage of the polar group on the water.

(4) Highly unsaturated acids, with three and five double bonds in the chains, behave very much like oleic acid, which only has one double bond.

(5) Archidic acid and its derivatives behave normally.

(6) The transition between the two "allotropic" condensed films of urea derivatives is examined more closely than hitherto, on eicosyl urea.

(7) Substituted acetamides show a solid film with chains close-packed at low temperatures, and this melts at a definite temperature, raise dby compression, to a liquid film of area 24.2 sq. A.U. It is probable that this meeting is due to the molecules acquiring sufficient kinetic energy other than translational, that is, rotational, about a vertical axis, or possibly vibrational, to break up the solid structure.

(8) Hydrocarbon chains, more than 27 carbons long, tend to mask the typical phenomena in condensed films, and probably have some tendency to pull the molecules out of the films.

(9) Pentærythritol tetrapalmitate, which has four chains attached to a common centre through polar groups, and should normally have these chains directed to the corners of a tetrahedron, orients all the chains vertically in the surface. These are not quite close-packed until a compression of about 20 dynes per centimentre is applied, this force being apparently necessary to strain the valency linkages from their normal direction to the necessary amount.

T. ALTY: *The Cataphoresis of Gas Bubbles in Water.* Communicated by Sir Joseph Thomson, F.R.S.

The chief results of this work are:—

(1) The velocity of a gas bubble in water is independent of the gas used.

(2) There is a great variation of velocity with the diameter of the bubble, the maximum velocity being 4.1×10^{-4} cm./sec./volt/cm. at a diameter about 0.1 mm.

(3) The velocity is proportional to the applied field throughout the whole range of diameters.

(4) The bubble does not acquire its full charge immediately on being introduced into the water.

(5) The rate of absorption of the bubble has a great influence on its velocity.

(6) The bubble only attains its highest velocity in water of specific conductivity 8.5×10^{-6} ohms^{-1}.

(7) In water of specific conductivity 1.8 $\times 10^{-6}$ ohms^{-1} the charge on the bubble is very small, and is occasionally reversed during the course of an experiment.

(8) Two bubbles appear to repel each other.

The structure of the double layer was discussed in the light of the above results.

Papers read in title only:—

D. R. HARTREE: *Some Relations between*

the Optical Spectra of Different Atoms of the same Electron Structure. I—Lithium-like and Sodium-like Atoms. Communicated by Sir Ernest Rutherford, F.R.S.

Relations between values of corresponding terms of the spectra of different atoms of the electron structure are worked out for the Bohr atom model with a central field. The relations are different according as the series electron does or does not penetrate into the core.

P. A. C. Dirac: *The Conditions for Statistical Equilibrium between Atoms, Electrons and Radiation.* Communicated by Sir Ernest Rutherford, F.R.S.

The principle that every process which occurs in an assembly in thermo-dynamic equilibrium is exactly balanced by the reverse process occuring to the same extent is applied to the general case of n-body encounters, both radiative and non-radiative processes being considered. Reaction equilibrium conditions are obtained involving the probabilities of the direct and reverse processes. It is shown that van't Hoff's isochore is of universal validity, even for radiative processes and with relativity mechanics.

From Planck's law of radiation it is deduced that every process by which radiation is emitted is stimulated by external radiation of the same frequency, the ratio of stimulated to spontaneous emission being independent of the nature of the process, and inversely proportional to the cube of the frequency.

The method is applied to the deduction of formulæ for the degree of ionization of a gas.

Ida Doubleday: *Boundary Lubrication.—Further Consideration of the Influence of the Composition of the Solid Face.* Communicated by W. B. Hardy, Sec. R.S.

Christina C. Miller: *The Stokes-Einstein Law for Diffusion in Solution.* Communicated by Sir James Walker, F.R.S.

In order to test the validity of the Einstein-Stokes equation for diffusion in liquids, the diffusion-coefficient of dilute solutions of iodine. These included both organic solvents and aqueous solutions of alkali halides. The experiments were carried out partly in a thermostatic bath, and partly in a cellar of nearly constant temperature. Determinations of the viscosity of the solvents employed were also made.

According to the Einstein-Stokes expression, which is based on the assumption of large particles moving amongst relatively small molecules, the product [diffusion-coefficient × velocity] should be constant for all solvents. The product in the case of organic solvents actually varied between 850 and 1,544; for aqueous solutions of alkali halide of different concentrations the variation was between 826 and 1,216. According to Sutherland, on the opposite assumption that small dissolved molecules move amongst relatively large molecules, the value of the product in the extreme case should be 1.5 times as great as the value given by the Einstein-Stokes expression. If acetylene tetrabromide be accepted, the ratio for any two products actually falls between 1 and 1.5. Attempts to correlate the value of the product with various physical properties of the solvent led to no vents of the same type some regularities definite general results, although for solvents of the same type some regularities were observed.

The product was found to be proportional to the absolute temperature within the experimental error, as it should be according to the expressions of Einstein-Stokes or Sutherland.

Helen S. French and T. M. Lowry, F.R.S. *Studies of Co-ordination. Part I. Absorption Spectra and Co-ordination of some Cupric Compounds.*

(*a*) The absorption-spectra of the cupric compounds, both organic and inorganic, are dominated by (i) a red or infra-red band, which is characteristic of the cupric atom and (ii) an ultra-violet band or general absorption, which depends mainly on the anion or organic radical. The colour of the cupric compounds depends on the character of the narrow region of transmission between these two absorptions.

(*b*) The conclusion is drawn that all the cupric cmpounds investigated are co-ordinated; but that whilst some of the organic compounds are stable towards water, others are decomposed by it, yielding a hydrated cupric ion, which, however, is also coordinated.

L. F. Bates: *On the Range of α-Particles*

in Rare Gases. Communicated by Sir Ernest Rutherford, F.R.S.

The range of α-rays in all the rare gases has been found by a scintillation method, in order to determine the nature of the agreement between the values found by experiment and those calculated by R. H. Fowler on the basis of Henderson's theory of the loss of energy of an α-ray in passing through matter. The value found for helium, after repeated purification of the gas used, is very different from that found by previous observers, due probably to the big effect of small quantities of impurities in reducing the range. It is found in these experiments that Henderson's theory, whilst accounting for approximately the same fractional loss of energy in all the rare gases, does not account for the whole loss.

There is a rough linear relation between the logarithms of the observed stopping powers and the logarithms of the atomic weights of the rare gases, but it does not take the simple form given by Bragg and Kleeman.

D. H. Black: *The β-Ray Spectrum of Meso-thorium 2.* Communicated by Sir Ernest Rutherford, F.R.S.

As the detailed study of the magnetic β-ray spectra of radioactive bodies has become of increasing importance in recent years, an analysis of the β-ray spectrum of mesothorium 2 was undertaken. Using the well-known focussing method, thirty-one lines were detected and their energies calculated. That it has been possible to classify the majority of these lines as being due to the conversion of γ-rays in the absorption levels of the atom itself lends further support to this theory. In all eight γ rays have been classified, and it has been possible to account for seven of these quite satisfactorily by the system of transitions between levels in the nucleus.

J. Keith Roberts: *The Thermal Expansion of Crystals of Metallic Bismuth.* Communicated by Sir Joseph Petavel, F.R.S.

R. Stonely: *Elastic Waves at the Surface of Separation of Two Solids.* Communicated by Prof. H. F. Baker, F.R.S.

J. H. Jones, Ph.D. and J. C. Boyce, M.A.: *The Constants of the Rydberg-Ritz Equation.* Communicated by Prof. O. W. Richardson, F.R.S.

The type of atomic field necessary to give observed terms in hydrogen-like spectra must be due to a virtual attracting charge *which is additional to the net charge of the* atomic kernel. The additional field, strong near the kernel, but rapidly diminishing at greater distances, resembles that of an electric doublet. Sommerfield's atomic model of coplanar rings gives a doublet of the wrong sign if Bohr's total quantum numbers are taken, but if his model is generalized to a spatial one, general conditions of orientations of the rigid orbits can be given. However an average orientation of the screening orbits seems more probable, which on this gasis would give no additional field.

It seems more likely that the doublet is induced in the kernel by the field of the valence electron itself, in its interaction with the screening electrons. This can be pictured as the charge induced on a conducting sphere, and for such a model a Ritz spectral forfula may be derived.

The radius of the equivalent conducting sphere is taken as that which would give rise to the same dielectric constant and is obtained from an expression for the dielectric constant recently derived by one of the writers from the theory of the Stark effect. From such a radins and known constants one of the correcting terms of the Ritz formula has been obtained for a number of spectra of the sodium type. The values obtained are found to be of the same order of magnitude as those calculated from known spectral data.

THE OPTICAL SOCIETY.

At a meeting of the Optical Society, held at the Imperial College of Science and Technology on Thursday, 13th November, 1924, the following papers were presented and discussed:

The Theory of Neutralization, by T. Smith, M.A., F.Inst.P.

Reasons were given for rejecting the current theory of neutralization, and a new theory which represents the experimental procedure more exactly is propounded. It is shown that the test should be made with the lenses midway between the test object and the observer's eye, and that the connection between the vertex powers of the lenses when neutralization is exact involves the

distance of the test object and the order in which the lenses are placed. From the discussion of numerical results it is concluded that the simple law of the zero sum for the vertex powers is attained with ample accuracy as a mean result, the combination of high-powered lenses of equal and opposite vertex powers appearing as a positive lens from one side and negative from the other. The theory leads to the suggestion that in practice plano-lenses should be tested with their plane, not their curved, surfaces in contact.

The back vertex power of a combination of lenses, by T. Smith, M.A., F.Inst.P.

The general relations between the constants o fa compound instrument and those of its components are obtained when the imagery is collinear. From these relations the expression for the vertex power of a compound instrument is built up in the form convenient for application in spectacle calculations. The formulae have other applications.

A New Type of Nephelometer, by R. Kingslake, A.R.C.S., B.Sc.

A new type of Nephelometer is described which provides an accurate optical method of measuring a minute amount of precipitate by means of the turbidity it produces in solution. Light is passed into the end of a tube containing the solution, and the intensity of the scattered light is measured by a special form of wedge-photometer. A description is given of the means by which stray light can be kept from the eye during observations, and an actual example is described illustrating the use of the instrument.

A Note on nephelometry, by Professor Alan Pollard, A.R.C.S., A.M.I.E.E., F.Inst.P.

The investigations which led up to the development of the nephelometer, an improved design of which is described by R. Kingslake, are briefly referred to. It is shown that the instrument is capable of measuring such minute quantities as the amounts of the oxides of nitrogen evolved from explosives in unit time under normal temperature and pressure. The original instrument is described as well as a nephelometer in which the usual prism train for producing the photometric field is replaced by two internal reflecting elliptical cylinders.

Exhibits.

Messrs. R. and J. Beck Ltd. demonstrated:—

(1) A high power dark ground illuminator for the microscope, which is provided with a focussing motion whereby it can be used on slips of any thickness from $\frac{1}{3}$ mm. to $1\frac{1}{2}$ mm. On slips as thin as $\frac{1}{3}$ mm. it can be used with object glasses having an aperture of 1.2N.A., on thicker slips with object glasses of numerical aperture of 1 N.A. or less.

2. An Aplanatic Ring Illuminator, which can be used for opaque objects with object glasses up to 4 mm. in focus. It reflects back to an aplanatic focus upon the object a large beam of light thrown upwards by the ordinary mirror of the microscope.

3. A Vertical Illuminator, which throws light through the object glass upon an opaque object. Either transparent or opaque reflectors, flat or curved and of varying shapes can be used and for the first time a complete set of adjustments is provided for tilting or moving the reflectors in all directions.

4. A simple form of Apertometer for measuring the numerical aperture of object glasses.

5. An experiment showing glare, illustrating the disadvantage of a large source of illumination.

6. A new form of Inverted Microscope and camera, on an optical bench for metallurgical work. This is arranged for almost simultaneous observation and photography, and can also be employed with short focus photographic lenses. It is specially noteworthy for its unusual rigidity and the improved design of its delicate adjustments.

7. A very small travelling microscope "The Baby London," which can be readily put in the pocket.

Professor F. J. Cheshire, C.B.E., gave a demonstration of the Abbe diffraction theory as predicted by Fraunhofer in 1832.

Mr. B. K. Johnson exhibited and desribed a convenient type of bench, designed and constructed at the Imperial College for the testing of large aero lenses.

THE INSTITUTION OF ELECTRICAL ENGINEERS.

Wireless Telegraph Valve Transmitters Employing Rectified Alternating Current, by G. Shearing, B.Sc.

The development of some of the valve

transmitters employing rectified power for naval purposes, from December, 1918, onwards, were described. The earlier work was briefly reviewed and general considerations of design for ship conditions were discussed.

The method of calculation of the geometry of the rectifying valve electrodes and of the power loss was given as well.

Some of the types of transmitter circuits employed were described and also detail circuit improvements for satisfactory working.

Arrangements of valves in series and the use of coupled circuits for drying-out wet aerial systems, also separate grid-excitation circuit arrangements, were dealt with.

Experimental circuits for the reduction of harmonic interference, also the arrangements adopted for signalling by grid potential control, were discussed.

Finally, the design of the transmitting valve electrodes is dealt with and the question of valve rating was discussed.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

Fuel Oil Resources of the Future, by ALFRED W. NASH, B.Sc., M.I.Mech.E., and H. G. SHATWELL, B.Sc.(Vict.), M.Sc.(Tech.), A.I.C.

Practically since the inception of the Petroleum Industry the availability of future supplies of mineral oil has been the subject of scepticism analogous to the opinions expressed from time to time regarding the future of the coal industry of this country.

Whilst petroleum or bitumen is known to have been used 300 years B.C., nevertheless the petroleum industry is of comparatively recent growth; yet hardly is the commercial value of the fluid realised before doubts are expressed as to the continuance of supply.

Within recent years the production of oil has reached such staggering proportions as to cause many to anticipate the exhaustion of the mineral oil resonrces of the world in the near future.

The technical journals of America, which is the most highly-developed country so far as petroleum is concerned, ten years ago were seriously warning the country that the then rate of production of oil could not be maintained, and that a policy of conservation was imperative if the petroleum industry was to be saved from ruin. Excellent as this latter advice appeared then to be, the annual production of crude oil in the United States is now more than double that of 1913.

In 1921 the daily production from new oilfields alone amounted to, roughly, twenty-five thousand tons or nine million tons in the year. During 1923 no fewer than seven new oilfields were discovered, and this in a country which is not only well populated, but which is being constantly explored and prospected with the drilling bit.

The fact that America is now importing large quantities of oil from Mexico does not prove the rapid exhaustion of its own deposits, but simply that the demand has exceeded the present available supply in that country: the question as to the future source of mineral oil, therefore, so far as America is concerned, is one which, in the author's opinion, need not give rise to immediate disquietude.

Assuming the present-day commonly accepted theory as to the origin of mineral oil to be the correct one, then the existing supplies of petroleum cannot be expected to last for ever any more than the reserves of coal can be expected to do.

It should be borne in mind, however, that, despite the rapid strides which the science of Petroleum Technology has made dnring its very short career, a greater advance in the time perhaps than any other applied science can show in its history, there are, in all its branches, with the possible exception of the engineering side, considerably more problems which remain to be solved than have been elucidated.

Before it can be stated definitely that the world's supply of petroleum will soon become exhausted, the following points, among others, need to be definitely established.

(*a*) That all the free petroleum which the earth contains has been located.

(*b*) That the problem as to the origin of petroleum is general, and each class of oil in particular, has been solved.

(*c*) That oilfields can be discovered and not simply located as a result of surface workings hy local inhabitants.

In attempting to allay any uneasiness which appears to exist in the minds of many as to adequacy of fuel oil for the next few generations, it is not intended to suggest that scientific and technical researches,

such as have been indicated, should be left to posterity. On the contrary it is definitely asserted as a considered opinion that it is is our duty to posterity to probe every possible expedient which presents itself for the conserving and supplementing of our existing supplies of fuel oil in order that the difficulties of the future may be, at any rate, partially if not completely solved.

The Somerset Oil-Shales, by H. G. SHATWELL, B.Sc. (Vict.), M.Sc. (Tech.), A.I.C., ALFRED W. NASH, B.Sc., M.I.Mech.E., and J. IVON GRAHAM, M.A., M.Sc., A.I.C.

The occurrence of oil-bearing shales in Somerset has been described by Dr. Forbes Leslie, who has conducted an investigation into the extent of the deposits and has given some detailed information regarding the nature of the shales, their distillation and the properties of the resulting oils.

In view of the importance of any new discovery of oil shales, it is of interest to inspect the Somerset deposits, to collect samples of the shale and to examine them from the standpoint of oil, gas and ammonia yields; and further to ascertain whether the spent shale would be suitable for use as cement.

Six samples of shale were taken. Quarrying was actually in progress so that the materials obtained were unweathered and each portion represents a fair average specimen of the five seams outcropping at Kilve.

An account of the distillation of the shale and an examination of the distillates was given.

The crude distillates were refined and the yield and properties of the refined products were as follow:—

Fraction.	Yield on original oil. Per cent.	Refinery losses. Per cent.	Sp. gr.	Sulphur. Per cent.
Light Naphtha	1.10	46	0.778	2.06
Heavy naphtha	2.20	27	0.816	2.52
Light kerosene	9.90	26.8	0.845	2.33
Heavy kerosene	8.80	48.7	0.880	2.65
Residue (unrefined) ...	—	—	0.973	2.60

ROYAL INSTITUTION.

A General Meeting of the members of the Royal Institution was held on December 1, Sir James Crichton-Browne, Treasurer and Vice-President, in the chair.

The special thanks of the members were returned to Dr. H. Rushton Parker for his donation of £100 towards the improvement of the Library. Professors Theodore Lyman, of Harvard University, and Gilbert N. Lewis, of the University of California, were elected Honorary Members, and Professor E. N. da C. Andrade, Mrs. M. H. Daniell, Dr. G. C. Simpson, Dr. D. P. Subotic, and Mr. W. J. U. Woolcock were elected Members of the Institution.

ROYAL SOCIETY OF ARTS.

On Dec. 8th, the third Cantor Lecture, entitled "Modern Colour Problems," was delivered by LOUIS C. MARTIN, Esq., D.I.C., A.R.C.S., D.Sc., Lecturer in the Department of Optical Engineering and Applied Optics, Imperial College of Science and Technology, South Kensington.

THE OPTICAL SOCIETY.

DEC. 11.

The following papers were presented and discussed:—

The Transformation of trichomatic mixture data, by J. GUILD, A.R.C.Sc., F.Inst.P., F.R.A.S.

An equipment for visual spectophotometry, by J. GUILD, A.R.C.Sc., F.Inst.P., F.R.A.S.

A simple micro-photometer, by. L C. MARTIN, D.Sc., A.R.C.Sc., F.R.A.S.

The following apparatus was exhibited:—

(*a*) *A telescope support*,

(*b*) *A prism holder for vertical protection*, by C. V. BOYS, F.R.S.

Slow speed precision training gear governed from a distance, by DR. P. P. SCHILOVSKY.

THE CHEMICAL SOCIETY.

DEC. 4.

Papers read:—

New halogen derivatives of camphor. Part VI. β-Bromocamphor-α-sulphonic acid, by H. BURGESS and T. M. LOWRY.

A series of α-sulphonic derivative of camphor was described. Since these were only obtained when a halogen atom occupies the β-position, the view that β-bromocamphor and Reychler's camphorsulphonic acid contain the substituent in the same position is considerably strengthened.

New halogen derivatives of camphor. Part VII. The constitution of the Reychler series of camphor-sulphonic acids. Experiments on chlorsulphoxides, by H.
α-Bromocamphor-π-chlorosulphoxide has
. BURGESS and T. M. LOWRY.
been prepared from the π-sulphonyl chloride and oxidised to *trans*-camphor tricarboxylic acid. Under the same conditions o-toluenesulphonyl chloride does not give a corresponding chlorosulphoxide.

The conversion of a sulphonyl chloride to a chlorosulphoxide takes place when the sulphonic group is linked to methylene, and not as a result of eliminating water with a neighbouring methyl-group.

The conclusion is drawn that no migration occurs during the formation of ketopinic acid from Reychler's camphorsulphonyl chloride, and consequently that the sulphonic group must be in the 10-position as stated by Wedekind.

Some co-ordinated compounds of the alkali metals, by N. V. SIDGWICK and S. G. PLANT.

The action of alkaline hydroxides on ψ-indoxyl*spirocyclo*pentane gave a substance MB, HB (M=Li, Na or K; HB=I) in which one metallic atom replaces one hydrogen atom in two molecules. The sodium and potassium derivatives lose one molecule of HB on heating. There can be little doubt that the first product MB, HB contains a 4 vo-valent metallic atom. The indoxyl ring admits of co-ordination between a metal replacing the imde hydrogen and the carbonyl oxygen, with the formation of the typical chelate ring of 6 atoms with two conjugate linkings.

The remarkable solubility in toluene is thus explained, since the compound is not a salt. The sodium has its octet completed by means of three pairs of shared electrons borrowed from the two oxygens and the now quadrivalent nitrogen. The second ring, being attached only by co-ordinate linkings, is easily removed, and hence the compound dissociates on heating.

A method of determining the presence or absence of complex salts in ions in dilute aqueous solutions, by W. H. PATTERSON and J. DUCKETT.

Ions may be arranged in a series, nearly identical with the Hofmeister series, and thus the effect of any simple salt (essentially soluble in water only) in raising the critical solution temperature may be foretold.

If, *e.g.*, 0·1 mol. of one salt and 0·1 mol. of another salt (per 1000 gms. of total solution) are added to the phenol-water mixture, and no complex occurs, the critical solution temperature found is the mean for 0·2 mol. of each salt separately. If a complex is formed in solution the rise in temperature will in general be above that of either and is a measure of the equilibrium.

Simple mixture was found in the case of the following:—

NaCl, KCl: KCl, LiCl.
$MgSO_4$, K_2SO_4 (schoenite)
$MgSO_2$, Na_2SO_4 (astrakanite)
$MgSO_4$, WCl (kainite).

Complex formation:—

HgI_2,KI
Alums
Sodium ferrioxalate
Sodium ferriocyanide.

NOTICES OF BOOKS.

L' Energetique des Réactions Chemiques, by G. URBAIN. Paris: G. Doin. 1915. Pp. 267, 102 figures. (Collection Langevin-Perrin-Urbain).

This physico-chemical text-book of Prof. Urbain's lectures at the Sorbonne possesses all the great advantages of having heen written by a great chemist and teacher, inventor and discoverer, thinker and philosopher. The obvious aim of the book is to introduce the chemist into the science of thermodynamics so that he will be able to use it advantageously for the treatment of purely chemical prohlems, and to this end the author has employed the minimum of necessary abstract reasonings. These are explained in the first part of the book, where great care is taken to deduce the fundamental laws hy strictly logical reasoning, distinction heting always drawn when empirical laws have to be brought in. Here as well

as throughout the whole book the high noëtical attitude of Prof. Urbain's treatise is one of its original features of rare value.

Much more attention than in books of a similar scope hitherto written is given to real irreversible processes, so abundant in the ordinary chemist's experience, and a clear treatment of such, as well as of the really reversible phenomena, is based on Prof. Urbain's system of isentropes (adiabatics) and isotherms (chap. IV.) Here, in a masterly, simple, and original way, the author handles his diagrams to derive the general laws of shifts of equilibria; is able to introduce the idea of absolute temperature even before ideal gases are mentioned; and comes to suggestive conclusions (Chap. V.) respecting compressibilities of isomers possessing different free energies.

Whilst the second part of the book deals with the necessary minimum of thermochemistry (the first is denoted as "introductory"), the third, undoubtedly more important, and certainly the chief part of the book, is devoted to modern doctrine of affinity. Here the experienced teacher gives *the student a rigid foundation of the present* state of knowledge to enable him to pursue the chief theoretical aim of every chemist, *viz.*, to understand rightly and to express exactly what is meant by chemical affinity. Especially in the brilliant opening chapter "La constrainte chimique et la catalyse," *does the true chemical sense of the author dominate; opening to a reflecting reader new* horizons and pointing out—with a certain scepticism—much that is new about "true" and "false" equilibria. He also discusses the vast field of stable organic isomers and their special destructive catalysers. The author's original and precise conception of "*l' état de la constrainte chimique*" *(state of chemical tension*, which remains latent when uncatalysed) brings much simplification even into the carrying out of reversible cycles, where the exact moment at which to introduce the suitable catalyst is never omitted.

Prof. Urbain's great esteem for Le Chatelier reflects itself in Chap. II., where mobile equilibria are treated very fully, systematically and with many interesting details of this important principle, whereas Chap. III. brings us to the definition of affinity by means of the mass-action constant with applications to gaseous dissociations, to which France has contributed so much.

Electrochemists will find special delight in the concise but clear Chap. V., where Prof. Urbain presents a few of the most fundamental conceptions better than in any of the original German sources and proceeds to deduce Nernst's potentials from a simple idea of ionic partition between the metallic and solution phase.

The systematic discussion of all possible changes of gaseous dissociations with temperature in succeeding chapters is again *novel and likely to be of a great practical* value.

Chapters VIII. and IX. deal with the phase rule and the classification of heterogeneous systems; the prominent feature in these reasonings being the rigid proof of the Rule itself, so often superficially deduced; Prof. Urbain operates here with the thermodynamic potential and entropy besides the ordinary factors of temperature, volume, pressure and mass, in such a simple way, that the law can be deduced—after preliminary considerations of phase-potentials—in one line.

The work concludes with a chapter on *Nernst theorem*, where the logical simplicity and originality of explanations, which characterises every line of Prof. Urbain's works and which is best understood from his own words in the preface (p. vi.)—not less interesting than the text-book itself—"thermodynamics made easy by a chemist for chemists."

J.H.

Patents Invention and Method, by HAROLD E. POTTS. Pp. 160. London: The Open Court Company, 149, Strand, W.C.2. Price 3/6 net.

This consists of six chapters, three of which have, we learn from the preface, been reprinted from three esteemed contemporaries, while three others are papers which were read beore the Chartered Society of Patent Agents. There is a very useful explanatory preface, extenting to some 20 pages. The papers, it might he added, range over a period of 72 years of Patent Practice, during which time the Editor of the works says that three problems struck him: The Criterion of an Invention, The Definition of an Invention, and The Evolution of an Invention. It is an informative and readable book.

The Elements of Colloidal Chemistry, by ERWEIN FREUNDLICH, Translated hy

GEORGE BARGER, F.R.S. Pp. 210. London: Methuen & Co., Ltd. 1924. Price 7/6 net.

This is a standard work by a well-known author, and is a non-mathematical introduction to an important subject, and cannot fail to be helpful to Students of Chemistry Physics and a longe range of subjects. Professor Barger's translation will be reliable, as might be expected, the intent of the original being faithfully produced in the translation.

There is given a very complete Alphabetical Index, which naturally enhances the value of the book, facilitating reference and thus saving the time of the student.

The chapter on Mists and Smokes has particular interest for those inhabiting large cities and industrial centres: " Mists and Smokes are Colloidal-disperse structures in which the dispersion medium is gaseous, while the disperse phase consist of droplets (in the case of mists) or of solid particles (in the case of smoke). . . The particles of coarse mists and smokes are deposited under the influence of gravity. Here the other influences, such as that due to the electrical charge, become negligible, but in colloidal-disperse mists and smokes they play a real part. There is a further complication in the case of mists, since they may disappear, not only by the increase and consequent settling of their particles, but also by complete evaporation; thus an aqueous mist may disappear in a sufficiently dry space.

" If for any reason evaporation is prevented, the remarkable case occurs, of a mist persisting in dry air. This is the cause of the extraordinary stability of the notorious London fogs. There droplets are coated with soot and with films of oily liquids, resulting from imperfect combustion of coal; this envelope prevents evaporation to such an extent, that the fog persists in a space which a hygrometer shews to be sensibly dry."

New Patents.

This list is specially compiled for *Chemical News*, by Messrs. Rayner & Co.. Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

28021 28022—Atlantic Chemical Co., Ltd. — Manufacture of concentrated borate from crude borate of lime. Nov. 22nd.

27928—Blumenfeld, J.—Filtration of solutions etc. Nov. 21st.

27449 27450—Mills, W. G.—Chambers for manufacture of sulphuric acid. Nov. 17th.

27567—Soc. Chemique des Usines du Rhone.— Process for manufacture of malonic acid esters. Nov. 18th.

Specifications Published This Week.

202970—Constant, G., and Bruzac, A.—Process of and apparatus for the reduction of metal oxides with continuous regeneration of the reducing gas employed.

206498—Ramsay, H. G. A.—Method of producing oxides of nitrogen.

224468—Bernard, G.—Process for the enrichment or other treatment of phosphated chalk and other substances with a basis of carbonate of calcium or lime.

224438—Badische Anilin & Soda Fabrik.—Production of alkali cyanide.

Abstract Published This Week.

222587—Recovering ammonia from gases.—Bone, W. A., Montrose, Harpenden Road, St. Albans, Hertfordshire, and Finch, G. I., 10, Gainsborough Mansions, West Kensington, London.

Ammonium phosphate; ammonia.— Ammonia is removed from gases containing it by passing the gas through a solution acidified with phosphoric acid or ammonium dihydrogen phosphate under such conditions that crystals of diammonium hydrogen phosphate separate, the operation being performed in a manner similar to the treatment of such gases with sulphuric acid to obtain ammonia and the acid phosphate which is used again. The heating of the diammonium phosphate may be effected with superheated steam the degree of superheat being so chosen that on cooling the issuing ammoniacal vapour the ammonia condenses to a concentrated solution with the water condensed from the steam present.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

Publisher's Announcements.

The following Books can be obtained from Rea & Inchbould, Merton House, Salisbury Square, London, E.C.4. :

CONFESSIONS OF GREAT SOULS,

By the Rev. J. E. Roscoe, M.A.

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An invaluable book for all who desire to excel as speakers and who wish to reason convincingly.

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CHEMICAL NEWS, MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

A NOTE ON "THE SIGNIFICANCE OF THE ELECTRODE POTENTIAL."

By J. HEYROVSKÝ, D.Sc., Ph.D., Charles' University of Prague.

In a recent number of *The Chemical News* (1924, CXXIX., 294), Mr. J. A. V. Butler replies further to the writer's answer (*The Chemical News*, 1924, CXXVIII, 357) of the criticism, which Mr. Butler has started elsewhere (*Proc. Roy. Soc., A.*, 1923, CIV., 667). Since his reply shows an entire misunderstanding of the present author's cycle and, on the whole, of the thermodynamic treatment of any cycle, exhibiting markedly where Mr. Butler is misled, opportunity is hereby furnished to define once for all the exact cause of the difference of opinion.

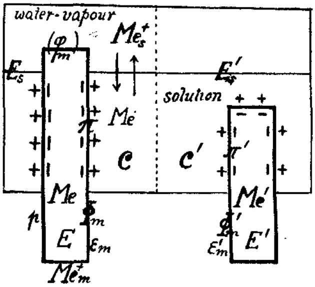
Let us deal directly with the principal condition, which unquestionably decides whether Mr. Butler's or the writer's idea is the only correct one, leaving aside arguments, whether the symbols can represent "free" or "total" energies; such differentiations could amount, practically, only to a few millivolts in the calculations, besides having nothing whatever to do with the final formula or soundness of the principle, by which the present author deduced the electrode potentials.

This crucial condition, accepted by both authors, is

$$\pi + E_s - \Phi_m = \frac{RT}{F}\log\frac{Me^+_m}{Me^+_s} \qquad (1)$$

Mr. Butler tries to uphold that Me^+_m (the pressure of the metallic ions over the dry isolated metal) is equal to Me^+_s (the concentration of unhydrated metallic ions imagined to exist in equilibrium in the water-vapour above the solution of the hydroxide Me OH) and believes to disprove the present author's E.P. formula on equating the sum of the potential terms of eq. (1) to zero. The present writer regards the two concentrations Me^+_m and Me^+_s as absolutely and principally different.

Since Mr. Butler is unable to see this from the author's communications, let us illustrate the cycle by the following figure.



In Mr. Butler's reply (l.c. p. 295, col. 2. 8th line) we read as an explanation of why the two concentrations Me^+_s and Me^+_m could be taken as identical "that there is no unique condition of equilibrium of ions between two phases" and from his following lines we understand that by the second phase Mr. Butler means the solution-vapour phase. Therefore his metal-vapour potential (ϕ_m) has to be placed into the surface of the metal protruding above the solution (see the fig., left half) and surrounded by the vapour of the solution.

This is where Mr. Butler is absolutely wrong. The present author has nowhere spoken of bringing the metallic ions out of the metal over the moist interface; on the contrary everywhere the transfer from the perfectly dry metal into its own dry metallic vapour was considered, and thus the true metal-metallic vapour interfacial potential ϕ_m must be placed outside the cell (see

ϕ_m in the fig.) and $Me\dagger_m$ above this *dry* surface.

If one falls into Mr. Butler's error, one can derive at once from a simple ionic transfer through the metal, vapour and solution equilibrium, that $\pi + E_s$ must be equal to Butler's ϕ_m (moist); in other words, $\pi + E_s - \phi_m = 0$.

Such a condition Mr. Butler should have been able to see immediately without his elaborate cycle, saving much valuable paper of the *Proc. Roy. Soc.* It is regrettable that Mr. Butler, starting quite correctly to take out the ions over the dry metallic surface into his first equilibrium box, where no water enters (*l.c. Proc. Roy. Soc.* p. 668, 3rd line from below), spoils later on his proof by bringing the electrons back into the metal another way *viz.*, over the moist interface (middle p. 669). It is here where Mr. Butler's fatal confusion of the moist *and dry interfaces starts and is completed* by his substitutions in the formula (I) (p. 670, 5th line).

Since, however, Me^{+}_{m} is an intrinsic property of the pure dry metal and Me^{+}_{s} only a function of the variable concentration of the hydroxide in solution, quite independent *of the presence or absence of the metallic* electrode, the absolute difference between Me^{+}_{m} and Me^{+}_{s} is unquestionable.

Mr. Butler will admit, that when we have to transfer the metallic ions from the dry surface of the metal, however distant from the solution, right into the middle of the solution-vapour, we need not consider his hypothetical " not unique condition of equilibrium of ions between the two phases " and regard his analogy with the salt MeX (*l.c.* p. 295) as meaningless.

The left-hand electrode (Me) of the fig. thus shows the unnecessary protrusion of the electrode into the solution-vapour, since the correct conception has to be derived from the right-hand half of the fig. (electrode Me′).

Finally, to explain to Mr. Butler from this figure what he has been unable to understand in the author's last reply, let us carry out the transfers between two electrodes of different metals Me and Me′:

1. Transfer of one gram-ion of the metal Me into its surrounding solution (π. F); the transport of one-half gram-cation from c to c′ and one half gram-anion in the reverse direction (work $(E_s - E_s')F$), disregarding the diffusion potential between the two solutions; the deposition of one gram-ion of *the second* metal on the electrode Me′ ($-\pi'$. F).

2. Transfer one F. of electrons from the first metal over the dry surface ($-\Phi_m$. F), condense it to the concentration of electrons existing above the second *dry metallic* surface (RT log ϵ_m/ϵ_m') and bring it into the *second metal* (Φ_m. F).

The result is that we have dissolved one gram-ion of the first metal and electrodeposited the equivalent of the second metal; thus the sum of the work terms in 1, and 2, must be equal to $(E' - E).F$, where E′ and E denote the real electrode potentials of the galvanic cell illustrated in the figure.

We have:

$$(E' - E).F = \pi.F + E_s.F - \Phi_m.F - (\pi' + E_s' - \Phi_m).F + RT \log \epsilon_m / \epsilon'_m$$

from which the electrode potential is given by

$$-E = \pi + E_s - \Phi_m + \frac{RT}{F} \log \epsilon_m + K.$$

Substituting from Mr. Butler's equation (I) (*l.c. Proc. Roy. Soc.*, p. 670), we obtain —as exactly indicated in the writer's last note (*l.c. The Chemical News*, p. 358) the author's formula for the electrode potential (*l.c. Proc. Roy. Soc.* p. 102).

Why this must be mentioned here is that Mr. Butler has nowhere stated to which of his potentias the real electrode potential, which he attempts to disprove, corresponds and it is consequently necessary to show him what relation his three potentials have to *the electrode potential E*, which in Butler's case of " zerosum " would have the absurd value

$$\frac{RT}{F} \log \epsilon_m \; !$$

SUMMARY:

The arguments of the writer's preceding note are illustrated by a figure and the illogical step, which Mr. Butler tries to uphold in his answer, is shown to lie in Butler's erroneous transfer of ions into the solution over the metal-solution-vapour interface, instead of bringing them over the dry metallic surface outside the cell.

THE ALEXANDRIAN SCHOOL.

By J. G. F. DRUCE, M.Sc. (Lond.), R.Nat.Dr. (Prague).

The Greek civilisation tended to spread further afield during the time of Philip of Macedon and Alexander the Great. When the latter's empire was disintegrated after his death in B.C. 323, an opportunity arose for the establishment of a school at Alexandria, which became the capital of Ptolemy's kingdom. The Ptolemys were all patrons of learning and a valuable library was collected at the " Museum of Alexandria."

A study of medicine and mathematics and astronomy soon flourished in this new seat of learning. Although the library was burned during the Roman conquest (B.C. 47) it remained the centre of learning until A.D. 415.

The theoretical speculations of the Greek philosophers were here brought into contact with the practical art of the working of metals practised by the Egyptians.

Euclid.—It was here that Euclid arranged and extended the mathematical knowledge of his day. Little is known of his life beyond that he lived around B.C. 300. Euclid discovered rigorous proofs of many theorems which before were unproved or only imperfectly proved. His " Elements " still serves as the basis of elementary geometry, indeed many of his actual proofs are still the best available. As he presented it to the Greeks at Alexandria, it consisted of thirteen Books. Only the Books I. VI. and XI. are extant. Euclid's work included a study of triangles, parallels, circles, areas, surfaces and solid geometry in connection with the volumes of prisms, pyramids, cylinders, cones and spheres.

How much of the " Elements " is Euclid's individual work is not known. It is certain that at least a large part of Book I. is due to Pythagoras. Hippocrates was responsible for much of Book III. and Exodus and later Greek mathematicians, also probably provided matter for the various Books of the " Elements." Whatever the source of the matter, Euclid's work greatly influenced the study of mathematics. His proofs, although occasionally tedious and clumsy, were strictly geometrical and complete, and this is probably the main reason why his system of treatment has survived for 2,000 years. Euclid also wrote other but less important treatises on various aspects of mathematics.

Archimedes.—Archimedes (B.C. 287-212) may be regarded as another member of the school at Alexandria although his home was at Syracuse. He was a mathematician and an engineer, and developed a study of mechanics — the beginning of Applied Mathematics.

The stories of his work in connection with the golden crown, the lever to lift ships, the terrifying engines of war, and of his death while drawing diagrams in the sand, are striking evidence of the struggle of a great mind with nature. He is the first man of pure science whose works have been handed down to succeeding generations. These works include not only his treatises on geometry and mechanics, but also his letters. They show a man of noble simplicity, full of appreciation for the work of others. He expressed a desire that his discoveries should be associated with those of Eudoxus, who had pointed the way to Archimedes' greatest triumphs, including the quadrature of curves and the comparison of solid volumes.

Eudoxus had proved that the cone was the third part of the circumscribing cylinder. Archimedes showed the sphere to be two-thirds. In the modern world, which can attack such problems by means of the far more expeditious calculus, this part of his work will be regarded chiefly as an example of great mental force and ingenuity.

Archimedes was the founder of the science of mechanics (including hydrostatics). He wrote several important books containing his own original work upon geometrical measurements. He calculated the value of π and obtained other data in connection with the circle, parabola, sphere and cylinder. His knowledge of mechanics enabled him to construct machines of war in which he made good use of the principle of the lever.

Archimedes accurately defined a fluid and discovered that when a solid body floats in any liquid, it sinks into the liquid just so far that the volume of liquid displaced displaced weights the same as the whole solid. This led to a further development, *viz.*, that when a body is immersed, wholly or partly, in any fluid, it appears to lose weight, and this apparent loss in weight is equal to the weight of the fluid displaced.

This principle (usually associated with Archimedes' name) enables us to find the density of substances.

Another name to be associated with his is that of Appolonius of Perga (about B.C. 260-200), who carried the work of the Greeks in pure geometry nearest to the conception of a generalised analytical treatment as established by escartes at a much later date. His great work was on the conic sections, whose general properties he worked out and to which he first assigned their present names, *viz.*, ellipse, parabola, and hyperbola.

The Alexandrine School also includes Eratosthenes (B.C. 275-194), who gave a statistical survey of the earth and made a map of the known world, attempting to introduce lines of longitude and latitude as well, and thus beginning a study of geography

(To be continued.)

General Notes.

BIOCHEMISTRY AND BIOLOGY.

Towards the conclusion of an informative article on Vitamines in Health and Disease in the November Indian Medical Record, A. K. M. Abdul Wahed, B.Sc., M.B., says that "during the latter part of last century startling discoveries were made in the realms of physiology, pathology, and bacteriology, but with the dawn of this century two new sciences, namely, Biochemistry and Biology, have not only made wonderful discoveries, but at the same time shaken the very foundation of pathology and bacteriology. So long we had laid much stress on the bacteria and halted long at the mile-stone of bacteriology but now there is a tendency not to believe so reverently the animal experiments; we now try to realise that man is distinct and there is a wide gulf of difference between man possessed of intelligence, personality, morality and spirituality and a dumb animal. So we now study man whether in disease or in health as quite separate and distinct from other animals. We have now attached different meanings to signs and symptoms which are nature's signals of danger, and also, at the same time, nature's attempt to cure. We are now trying to understand the clinical signs and symptoms and we are trying to investigate what are the pre-symptoms before the actual disease has broken out or advanced too far for human control. Thus there is a tendency to nip the disease at the very bud; hence medicine is now going to be used more for preventive purposes. Such are the teachings of Biochemistry and Biology and the questions of vitamines are only a chapter of Biochemistry.

"Twelve years ago the investigation of a biochemical problem, namely, the proteins of good biological value, led accidentally to the discovery of vitamines. Within six years most of our present knowledge about the vitamines was gathered and during the late war all the facts were verified. In the meantime hot controversies have been raged over the biology of one and all the deficiency diseases, and as a consequence we have got at present an extensive meaning of the deficiency diseases and our ideas too about deficiency of diet have been broadened. The deficiency diseases themselves, how vast each of them, how complex the etiology of each and how important and certain the rôle of the vitamines play in their causation and cure. Then the relation between endocrines and vitamines especially have opened a very wide vista for research.

"Regular growth and maintenance of health are the birth-right of every man. Nature wants perfection and health and resists disease to the utmost. The facts about vitamines point to these ends and let every one act up to these findings."

GAS UNDERTAKINGS IN GREAT BRITAIN.

The Board of Trade have issued Part II. of the Return relating to authorised gas undertakings in Great Britain for the year 1923.

The total nominal capital of the 785 undertakings dealt with in the return was £165,210,254 (including loans borrowed by local authorities and since repaid), showing an increase of more than £2¼ millions on the amount shown in the Return for 1922. The receipts of the undertakings on revenue account amounted to £67,576,358, a decline of £3,050,293 from the total for the previous year, and the expenditure fell by

£2,605,535 to £56,593,900. The gross margin of £10,982,458 was accordingly £444,758 less than the 1922 figure.

Companies' undertakings numbered 475, and their aggregate loan and stock or share capital was £106,597,760, of which £22,035,911 was loan capital. Their receipts on revenue account were £44,226,797, and their expenditure was £37,839,199, leaving a gross margin in 1923 of £6,387,598, or £369,285 less than in the preceding year.

Undertakings by local authorities numbered 310, and the total amount of money borrowed in respect of them was £58,612,494, of which £30,027,099 had been repaid or was held in sinking funds. The receipts on revenue account were £23,349,561 and the expenditure was £18,754,701, the gross margin of £4,594,860 being £75,473 below the amount for the previous year.

INDIAN COTTON RESEARCH LABORATORY.

On December 3rd the Viceroy laid the foundation stone of the Technological Research Laboratory. This will be the only laboratory in the world concentrating on the improvement of raw material and the investigation of growers' seeds.

BRITISH SHARE OF BOXER INDEMNITY FUND.

The President of the Federation of British Industries has written a letter to Mr. Austen Chamberlain, M.P., Foreign Office. The purport of the letter will be understood from the following :—

" The Federation feel most strongly that the question of the application of these funds is directly of the greatest importance to industry in this country, and they cannot help feeling that the Committee provided for in the China Indemnity Bill, as amended by the late Government, is not sufficiently representative of all the important interests involved to give adequate and impartial consideration to the various schemes which will doubtless be put forward for the allocation of these funds. Moreover, there exists, in the opinion of the Federation, a serious danger that a Committee including two representatives of education without the presence of representatives of other important interests would tend to prejudice the important questions of principle involved in the allocation of the funds.

" The Federation attach the greatest importance to the desirability of the Committee being able to give the fullest consideration to all suggestions which may be put forward, whether educational or otherwise, and they maintain that such consideration cannot be given except by a Committee on which industry and commerce are adequately represented."

NEW YORK ASSOCIATION CONFERENCE AT CHEMICAL EXPOSITION IN 1925.

A joint meeting of close to twenty technical and commercial associations, to be held in conjunction with the Tenth Exposition of Chemical Industries during the week of September 28th to October 3rd, 1925, at the Grand Central Palace, New York, is being planned. It is expected that a programme of common interest to members of all the associations will be worked out and that the big joint meeting will follow individual meetings of the various associations in New York during the week of the Chemical Exposition. Of course, the nucleus of the meeting will be formed by organisations of interests primarily chemical, while other groups including pulp and paper, glass and ceramics, leather and tanning, photography and photo-chemistry, metallurgy, methods of testing materials, materials of chemical construction and engineering, fertilizer and allied interests will be represented, according to the early plans.

As in previous years, during the week of the Chemical Exposition, the representatives of the chemical and allied industries moved *en masse* to New York, it is planned for the Exposition in 1925 to more or less organise this movement of chemical interests and broaden the appeal to various association members by the holding of a great joint conference. Only big broad problems of chemical production, distribution and consumption will be taken up owing to restricted time and the diversified interests of those attending the meeting. If the big meeting at the Exposition during Septem-

ber-October of next year proves altogether successful, the idea will probably be expanded in 1926 to a still larger conference of all chemical, chemical equipment and engineering, and the chief chemical consuming groups in this country.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE ROYAL SOCIETY.

THURSDAY, DECEMBER 4, 1924.

PAPERS READ.

1. A. Fowler, F.R.S.—The Structure of the Spectrum of Ionised Nitrogen.

New observations of the second line spectrum of nitrogen (N II or N+) have been made in the region $\lambda 6650$ to $\lambda 2200$, and 52 lines have been classified in relation to the terms which combine to produce them. In this region, all the terms which have been identified belong to singlet or triplet systems. These have been found to combine with each other in agreement with the selection rules which are applicable to other spectra in which p' and d' terms appear. The absolute values of the terms cannot yet be stated, but a value of 70,000 has been provisionally assigned to $2p$, in accordance with the value suggested for $1p$ by astrophysical data.

The largest term identified is a p term, and it may be inferred that the series electron in singly ionised nitrogen normally occupies a 2_2 orbit, so that the atom of N II has two electrons in 1_1 orbits, two in 2_1 and two in 2_2 orbits. From the spectroscopic displacement law it may be further inferred that this is also the probable arrangement of orbits in the neutral atom of carbon, the spectrum of which has not yet been resolved into series.

Three groups of lines which involve one of the p terms are remarkable as showing large displacements ($>$ 0·5 A) to the red in vacuum tubes containing nitrogen at relatively high pressures.

2. H. Jeffreys—On the Formation of Water Waves by Wind. Communicated by Prof. G. I. Taylor, F.R.S.

Kelvin's theory of the formation of water waves by wind, which supposed the motion in both air and water to be irrotational, has been found to lead to several quantitative predictions that disagree with observation. An alternative theory is developed in the present paper. According to this theory, the wind presses more strongly on the slopes of the waves facing it than on the sheltered slopes, and it is when the resulting tendency of the waves to grow is just able to overcome viscosity, that waves are first formed. A numerical constant in the theory can be adjusted to make the wind velocity required to produce waves agree with observation; and when this is done the predicted wave-length of the waves first formed agrees with observation without further assumption. Several other facts of wave-formation are readily explained by the theory.

An attempt has been made to account for the skin friction of the wind over the seas as the resultant drag due to the horizontal thrust of the wind on the exposed sides of the waves. Agreement with the ordinarily accepted value of the skin friction can be attained if the wave velocity is about three-quarters of the wind velocity, which is in accordance with observation. The formation of waves with such a velocity, however, appears to require values of the eddy-viscosity much smaller than are indicated by observations of ocean currents; thus there is an outstanding discrepancy.

3. J. E. Jones—On the Determination of Molecular Fields. III.—From Crystal Measurements and Kinetic Theory Data. Communicated by Prof. S. Chapman, F.R.S.

With the information obtained about argon in the preceding papers from its properties as a gas, theoretical calculations are made of the interatomic distances to be expected in argon as a crystal. Crystalline argon has recently been obtained, and its structure measured and examined, and it is thus possible by a comparison of theoretical and observed values to fix the molecular field of argon. Theoretical calculations are also made of interatomic distances in KCl and CaS which are in good agreement with observations.

4. J. E. Jones—On the Atomic Fields of Helium and Neon. Communicated by Prof. S. Chapman, F.R.S.

The atomic field of helium is determined from measurements on its isotherms and viscosity, that of neon from measurements of its viscosity, and heat conduction and the crystal constants of NaF and MgO.

5. F. S. Tritton—A Centrifugal Method of making Small Pots of Electrically Fused Refractory Materials. Communicated by Dr. W. Rosenhain, F.R.S.

The paper describes a method of making small pots of refractory materials (magnesia, alumina, zirconia and tungsten metal) by electric arc fusion combined with centrifugal action. The material, shrunk by previous fusion and finely powdered, is placed in a silica cup and a deep central depression is made in the powder. Two graphite electrodes fit closely into this depression. The cup, suitably mounted, is rotated at the beginning of the experiment at a speed of two revolutions per second, and an electric arc is struck. The current is increased together with the speed of rotation of the cup until the material begins to melt and the depression assumes a parabolic form. When sufficient powder has been melted, the arc is switched off; a pot has thus been formed, is allowed to cool, and is separated from the unmelted powder.

With magnesia pots no further precautions are needed, but in the case of alumina or zirconia, in order to prevent the formation of carbides, a stream of oxygen is blown between the electrodes and the refractories during fusion.

Pots of fused magnesia made in this way have been successfully used for holding molten iron oxide, which penetrates all other known refractories.

PAPERS READ IN TITLE ONLY.

6. J. W. Nicholson, F.R.S.—Spheroidal Wave Functions.

The paper develops a new class of solutions of the equation of wave motion in oblate spheroidal co-ordinates, which satisfies boundary conditions which can be made identical with corresponding conditions in problems of solutions of Laplace's equation. The new solutions are not of the form of products of functions of single "normal" co-ordinates appropriate to the spheroid, but they nevertheless can be applied readily to the exact solution—without the use of harmonic series, after the manner of Mathieu and others—of problems of diffraction of waves by circular discs.

7. J. V. Howard and S. L. Smith—Recent Developments in Tensile Testing. Communicated by Prof. W. E. Dalby, F.R.S.

When a steel test piece is pulled beyond a limiting stress, the removal and re-application of the load causes a loop to be traced in the load-extension diagram recorded by the Dalby autographic load-extension recorder. The extension which occurs when a loop is being traced is analysed into a proportionally elastic portion and a non-proportionally elastic portion. The latter is called recoverable slip. Recoverable slip is shown to depend only on stress; and it can be correctly measured by the mean width of the loop parallel to the extension axis whatever the dimensions of the test piece.

Experiments also show that permanent set is the ultimate cause of rupture, and that permanent set is caused by the act of looping.

Hence the stress required to produce a standard mean loop-width provides a means of comparing different steels as regards that property of the metal which is revealed by this method of testing.

The recovery of elastic properties with time is investigated. Under certain conditions of heat treatment and composition, no recovery takes place at ordinary temperatures; nor does steel recover if left in a state of stress.

Researches are recorded on the influence of variations in carbon, phosphorus, nickel and chromium on the looping properties of steel. Variations due to different heat treatments are also investigated. The tests reveal changes in the physical properties of the metal which are not indicated by the usual methods of testing.

8. F. C. Harris—The Photo-Elastic Constants of Glass as affected by High Temperatures and by Lapse of Time. Communicated by Prof. L. N. G. Filon, F.R.S.

1. *Temperature Effect.*—The stress-optical coefficients of several glasses, of known chemical composition, were measured at different temperatures up to 400 deg. C. With only one exception, the stress-optical coefficient of the glass was found to show

a general increase with rise of temperature. In the case of the one glass which showed a small decrease in the coefficient with rise of temperature, this glass was an extra dense flint, containing a high percentage of lead.

2. *Lapse of Time Effect.*—The stress-optical coefficients of a number of glasses were measured at atmospheric temperature, and the values obtained were compared with those determined some 17 to 20 years ago by Prof. L. N. G. Filon. The results seem to indicate that the stress-optical coefficient increases comparatively rapidly during the first year or two after being cast, and finally settles down to a steady value.

9. A. L. Narayan and D. Gunnaiya—Absorption and Dispersion of Thallium Vapour. Communicated by Lord Rayleigh, F.R.S.

The absorption of light by Tl vapour has been studied, and it has been found that the non-luminous vapour of the metal absorbs lines of sharp and diffuse series and that 1, π_2 orbit is the ground-orbit of the valence electron. At about 900° C. quite a large number of bands of diffuse and complex structure, and some lines, made their appearance, probably due to Tl_2 molecules.

The absorption of the vapour in the near infra-red has been studied both visually and photographically, and it has been found that the vapour does not exhibit any selective absorption in the region $0{\cdot}9\mu$ to $1{\cdot}35\mu$, and that therefore 1, $\pi_2 - 1$, π_1 is not the single-line spectrum of the metal.

The present work confirms the findings of H. Geisler and Prof. McLennan, that at $\lambda 5350{\cdot}6$ the vapour exhibits anomalous dispersion, though feebly. Further, the experiments of the authors indicate more prominently the existence of anomalous dispersion at $\lambda 3775{\cdot}7$.

10. R. d'E. Atkinson—Note on Vegard's Theory of the Aurora. Communicated by Prof. F. A. Lindemann, F.R.S.

I.—It is shown that the presence of solid nitrogen would not account for auroræ at great heights since (1) there probably cannot be a strong enough field to lift crystals; (2) the volume charge they would carry would be impossibly large if enough light were to be obtained; (3) the largest crystals that could by any means be lifted would probably be completely vaporised by one electronic impact; (4) solid nitrogen probably cannot emit a narrow line.

II.—The possibility of low enough temperatures is disproved.

III.—The experimental evidence of Vegard is shown to be inconclusive, and the only other evidence directly antagonistic.

IV.—Two alternatives, in which the aurora is explained as a purely gaseous luminescence, are outlined, and the possibility that the gas might be oxygen instead of nitrogen (as far as 5578 is concerned) is discussed.

11. M. Weinberg—The Spark Spectre of Indium and Gallium in the Extreme Ultra-violet Region. Communicated by Prof. J. C. McLennan, F.R.S.

The spark spectra of gallium and indium were examined in both quartz and vacuum-grating regions. Owing to the fact that gallium and indium oxidize very easily in air, their spectra in the quartz region were taken in hydrogen. There are altogether 107 indium lines in the quartz region, some of which are extremely faint. They extend over a range of 1885 to 2337 A.U. There are fewer gallium lines in this region. These range over 1855 to 2364 A.U.

For both elements the vacuum-grating spectrograph revealed a great mass of lines in the extreme ultra-violet. There were from 1,000 to 1,500 lines on one plate. On elimination of the impurities, however, it was found that there were 828 gallium lines ranging over region 157—2059 A.U., and 464 indium lines ranging over 161—2082. In gallium there were a few very faint lines extending as far down into ultraviolet as $\lambda = 126{\cdot}8$ A.U. These occurred on one plate only, and are questionable.

12. S. W. Richardson—The General Law of Electrical Conduction in Dielectrics. Communicated by Sir William Bragg, F.R.S.

13. T. Lewis—The Interpretation of the Results of Bucherer's Experiments on e/m. Communicated by Prof. G. A. Schott, F.R.S.

In this paper it is proposed to show that the whole of the traces obtained by Bucherer in his e/m experiments may be used in order to verify the mass formula for the electron. Bucherer, and also Neumann in his repetition of Bucherer's experiments,

have restricted their calculations to the points on the curves corresponding to the maximum deflection of the electrons, and in this way have verified the formula for velocities up to 0·80 of that of light. The paper takes account of all the rays which escape from the condenser and shows how to construct the trace on the assumption that the Lorentz mass formula is valid for all velocities. The actual calculation is confined to the extreme end of one trace (that for which $E/H = 0·5154$), which is produced by the electrons of high velocities, for it is in this neighbourhood, if at all, that one would expect the difference between theoretical and experimental traces to be most marked.

On comparing the experimental trace with the theoretical the conclusion is reached that the former, on the whole, may be taken as a confirmation of the validity of the Lorentz formula for high velocities provided electrons with these high velocities are emitted in *sufficient number to produce the desired* photographic effect. From the results it would seem that electrons must be emitted with velocities up to at least 0·94 of the velocity of light. This is higher than the velocities recorded by Ellis up to date, but well within the range observed by Danysz. However, it is desirable that a more detailed investigation of the β-ray spectrum of radium and its derivatives *should be undertaken, and also that Bucherer's experiments should be repeated.*

14. A. M. Mosharrafa—On the Quantum Dynamics of Degenerate Systems. Communicated by Prof. O. W. Richardson, F.R.S.

(1) A set of quantum restrictions is suggested for degenerate conditionally periodic systems, in the form :—

$$Y_j = \tau_j h$$

where Y_j is a specified "adiabatic invariant."

(2) The conditions are applied to the case of the hydrogen atom in the presence of an external electric field and are shown to lead to the adoption of "half-integral orbits" in the Stark Effect, already suggested by the present writer on other grounds.

(3) A further example of the application of the conditions is discussed. It is shown that they lead to completely consistent results. In particular *no discordant results concerning the orbits are yielded.*

(4) The relation of the hypothesis to the *general question of fractional quantum* numbers is pointed out. It is suggested that the origin of these fractions is to be sought in the mechanism of degenerate systems.

15. E. G. Dymond—On the Precise Measurement of the Critical Potentials of Gases. Communicated by Sir Ernest Rutherford, F.R.S.

1. The factors limiting the accuracy of previous measurements of excitation poten*tials are discussed.*

2. The application of automatic differentiation of the characteristic curves to increase the sharpness of the bends in them is described. The reasons for the divergence of the value found for the first excitation potential of helium, 20·9 volts, from that calculated from the optical data are discussed.

3. The problem of interpretation of the characteristic curves, taking into account *the variation in the probability of effective* collision and the velocity distribution of the electrons, is attacked.

4. Efforts towards finding the variation in the probability of effective collision and its numerical value are described.

16. I. Langmuir and K. H. Kingdon—*Thermionic Effects caused by Vapours of* Alkali Metals. Communicated by Sir Ernest Rutherford, F.R.S.

1. From thermodynamic considerations involving Saha's equation there must be a relation between the positive ion emission from a heated filament in the vapour of an alkali metal and the electron emission from this surface.

2. At high filament temperatures and low pressures of the vapour, electron emission is the same as in absence of vapour, so that positive ion emission from different filaments in various vapours can be calculated. Experiments with cæsium and other metallic vapours, and with tungsten filaments and oxygen-coated and thorium-coated filaments, give results in accord with this theory. Measurements of positive ion and electron emissions from tungsten filaments in cæsium vapour give values for thermal ionization at about 1,200° K., in excellent agreement with Saha's equation.

3. At high filament temperatures positive ion emission becomes limited by rate at which vapour comes into contact with fila-

ment, all atoms striking the filament being converted into ions. This permits quantitative measurements of vapour pressure to be made.

4. At lower filament temperature electric image force causes a fraction θ of filament surface to be covered by a layer of absorbed ions, which share electrons with the underlying metal. The resulting double layer causes increase in electron emission and corresponding decrease in positive ion emission. Electron emissions of over 0·3 amp. per cm^2 at 1,000° K. may be obtained in cæsium vapour 30° C.

5. The theory of dilute adsorbed films (θ 0·2) is developed. Equation of state for adsorbed film is found to correspond to ideal gas laws. For more concentrated films, attractive forces draw the ions together, and under certain conditions separate 2-dimensional phases appear.

6. Heat of evaporation of adsorbed cæsium atoms on tungsten in form of ions corresponds to 4·0 volts for dilute and 4·3 for concentrated films. From adsorbed oxygen on tungsten heat of evaporation of cæsium ions is 5·1 volts.

SOCIETY OF GLASS TECHNOLOGY.

A meeting of the Society of Glass Technology was held in the Coal Gas and Fuel Industries Department, The University, Leeds, on Wednesday, November 19th, 1924, the President, Col. S. C. Halse, in the chair. Four papers were presented and discussed.

(1) "Note on the Glasshouses of the Leeds district in the 17th, 18th, and early 19th Centuries," by Francis Buckley.

John Houghton, writing in 1691, stated that there were then three glasshouses in Yorkshire, one near Ferrybridge, and two near Silkstone. They could now identify these as the glasshouses at Houghton, Bolsterstone and Silkstone. Henry Fenny was in possession of the Glass Houghton factory in 1740, but by the end of the century the business had ceased. The glasshouse at Rothwell Haigh was erected before 1726. A good description of it appeared in the *Daily Post* for March 10th, 1726. From the Rothwell Registers it was fairly evident that the firm who took the glasshouse in 1726 included Stourbridge glassmakers. The last actual mention of the glasshouse was in 1773.

The only glasshouse actually in or near the town of Leeds in the 18th century was known as the Engine Glasshouse, and this was probably the factory that supplied all the ordinary needs of the town for the greater part of the 18th century. It could be traced between 1738 and 1770. The Engine Glass House might have been the present as well as the predecessor of the famous Hunslet Glass Works, though the connection had still to be proved. Between 1814 and 1861, at any rate, the Bower family had several factories here. The people of Leeds must have owed as much to this family in the 19th century, as they did to the Fennys in the previous century. In 1883 they had four glasshouses at work, and no competition in the town itself. Just before 1850, however, there was a sudden increase in the glass concerns in Leeds and the surrounding district, especially in the neighbourhood of Castleford.

An early 19th century glasshouse at Thornhill Lees could be traced back to 1830. Here Noah Turner made flint glass until the glasshouse was taken over by the Kilners before *1847*, and converted into a bottle works.

There was a glasshouse also at Worsborough Dale in 1833, worked by William Usherwood, but in the following year Messrs. Wood & Perkes were found in possession, making cut glass.

(2) "A Striking Instance of Fireclay Corrosion Through the Action of Saltcake," by Prof. W. E. S. Turner, D.Sc.

During the emptying of a glass tank, with the gas flame still running, the fireclay blocks surrounding the dog-hole in a bottle-glass furnace began to swell and to flow, soon after they became exposed to the action of the flame, as the tank was drained. There was a suspicion that when the tank was started a charge of saltcake had been put into the dog-hole, under the belief that the blocking of the hole would be prevented. After examination it was found that the exposed portion of the blocks had absorbed saltcake at an early stage in the operation of the furnace, and being covered with glass and the dissociation temperature very high, the saltcake had remained unattacked, until contact with the flame during

the emptying of the tank brought about decomposition.

(3) " A note on some Properties of a Sandstone Block after use in a Glass Furnace," by H. S. Houldsworth, M.Sc.

In the experiments described refractory material (Penshaw Stone) and glass were ground separately until they passed a 100 mesh I.M.M. sieve, and were then thoroughly mixed in the desired proportions. A little gelatine solution was added, and cones were shaped from the mixture. These were then heated alongside standard Seger cones in a gas-fired laboratory furnace. The results obtained indicated that powdered Penshaw stone interacted as readily with a soda-lime glass as did powdered or good fireclay bricks. Penshaw stone developed a close compact structure when used in a glass furnace. This tended to hinder the penetration of glass into the stone, thus adding to the life of the refractory, and pointing to its successful use in furnace construction.

(4) " The Production of Colourless Glass in Tank Furnaces, with special reference to the use of Selenium. Part IV. The Influence of Arsenious Oxide," by A. Cousen, M.Sc., and Prof. W. E. S. Turner, D.Sc.

Previous work by the authors had shewn the great influence of arsenious oxide in preventing the development of colour in a selenium decolourised glass. It was evident that some of the effect was due to the action of the oxide upon the iron present. In confirmation of this fact meltings of a glass batch with addition of various quantities of arsenious oxide were made, and the colour of the glass was found to be less the more of the oxide there was in the batch. This, then, was the first important effect of arsenious oxide in decolourising, the second consisted in the suppression of the brown selenium colour. From this point of view selenium and cobalt oxide were only secondary materials in the decolourising process. The pink colour due to selenium was developed at the commencement of melting. For its successful production it required a hot furnace for the first stages of melting, and a low iron oxide content of the glass. An attempt to replace arsenic by its equivalent of phosphorus in the form of calcium phosphate shewed the latter substance to have little or no effect upon the brown selenium colour. Antimonious oxide used instead of arsenious oxide with selenium gave a deep bluish green colour. The cobalt oxide required in decolourising was about 1/12 oz. per 1,000 lbs. of sand, and this quantity could not be increased by 50 per cent. without producing a distinct blue colour in the glass.

THE FARADAY SOCIETY.

Nov. 17.

THE KINETIC THEORY OF EVAPORATION.

By D. B. MacLeod, M.A., D.Sc.

The phenomenon of evaporation from liquids has long been explained by the kinetic theory, on the assumption that various molecules are moving with different velocities. At any given temperature, the faster moving molecules tend to escape, leaving the remainder on the average slower. If they all moved with the same speed, it is fairly obvious that the liquid would have no vapour pressure until all the molecules had sufficient speed to escape when the liquid would explode.

It is proposed to assume that the ratio of the density of the vapour above a liquid to the density of the liquid is really the ratio of the number of molecules with sufficient speed to escape from the liquid to the number with insufficient speed. Thus if Dv and De are the densities of the vapour and liquid respectively, then

$$\frac{Dv}{De} = \frac{Ns}{Ni}$$

where Ns is the number of molecules with sufficient speed to escape and Ni the number with insufficient speed.

It will be seen that the results which follow from this assumption are so simple and satisfactory as to make the truth of the assumption extremely probable.

VISCOSITY OF REVERSIBLE EMULSIONS.

By Shridhar Sarvottam Joshi.

Plateau had observed that increased viscosity and a low surface tension were essen-

tial for the stability of bubbles and foam structure. Stables and Wilson confirmed the rôle of viscosity in the case of saponin solutions, although the surface tension was comparatively high. Hillyer basing his views on Plateau's earlier work correlated the phenomenon of emulsification with the viscosity and surface tension effects due to the emulsifier. Pickering's well-known work seemed to reduce the value of the viscosity factory and the rôle of the emulsifier was considered more from the standpoint of its preferential wetting by either of the constituents of the emulsions. The importance of the viscosity data in the theory of emulsion-stability and emulsification, as well as in industrial practice, is evident.

In the previous paper in this series, working with water-in-oil emulsions, and using a monovalent soap as an emulsifier, the dependence of the permanence of these emulsions upon the viscosity of the oil-film was observed and further, that, the surface tension of these emulsions exhibited an abrupt change at the critical phase-ratio. It was suggested by the author in the above paper, that the film enveloping the dispersed globules persisted mostly unchanged throughout the successive phase-ratios and that its nature was altered at the neighbourhood of the reversal point, and hence the observed sudden change in its surface tension. In view of this dependence of the type as well as the stability of such emulsions, upon the presence of a viscous film and also on the volume-ratio of the phases, it was thought that a knowledge of the viscosity of these volume-reversible emulsions and the progressive variation in the viscosity, as the reversal point is approached and passed, would give not only a new method for the detection of the inversion point, but also it would give an insight into the structural and size changes affecting the dispersed globules before and after the reversal of the emulsion-type.

The emulsions were prepared by churning varying amounts of pure olive oil, castor oil (Morton's cold drawn), and paraffin oil (Merck's), with differently concentrated solutions of sodium oleate, potassium palmitate, oleate and stearate.

Viscosities of water-in-oil emulsions prepared from castor oil, olive oil, and paraffin oil by means of four monovalent soaps are determined. Viscosity increases with increase of the dispersed phase and is maximum at the reversal point which is followed by a sudden drop in viscosity upon inversion.

The concentration and the specific chemical nature of the emulsifying agent have no effect on the viscosity of the emulsion.

Hatschek's equation for the viscosity of the emulsoids is not followed; observed viscosities are in approximate agreement with those estimated by Einstein's equation for suspensoids; Arrhenius' equation applies better still. The possibility of an increment in the size of the grains of the water-in-oil emulsions with increase in the proportion of the aqueous phase is suggested.

THE HYDROLYSIS OF ALKALI CYANIDES IN AQUEOUS SOLUTION.

By

R. W. E. B. Harman and F. P. Worley.

The degree of hydrolysis of alkali cyanides in aqueous solution has been determined by several methods, but the results obtained by different investigators are far from concordant. None of the methods that have been used is free from disturbing factors which have probably affected the results obtained by the various methods to different extents. The method employed by one of us with V. R. Browne in which the vapour pressure of hydrogen cyanide over solutions of potassium cyanide was compared with that over solutions of hydrocyanic acid, appears to be freer from complications than other methods that have been used. Since, however, the results arrived at by this method were considerably higher than any previously obtained, it appeared desirable to carry out further investigations by the method, especially since we find that the degree of hydrolysis found at different temperatures is not in accordance with the accepted views of the effect of change of temperature on the displacement of equilibrium.

ON THE VISCOSITIES OF LIQUIDS AT THEIR BOILING POINTS.

By D. B. Macleod, M.A., D.Sc.

In an earlier paper on the relation between the viscosities of liquids and their molecular weights the author attempted to

show that at 0° and under conditions of equal free space, the viscosities of liquids were proportional to their molecular weights in the liquid state.

Van der Waals's equation of state requires that, at the critical temperature, the volume b occupied by the molecules, should bear the same ratio to the critical volume, namely, $v = 3b$, for all liquids. Further, the reduced equation of state requires that at corresponding temperatures and pressures, the volume occupied by the molecules should also bear the same ratio to the corresponding volume, for all liquids. Liquids, then, at corresponding temperatures and under corresponding pressures, should be in a condition of equal free space, and their viscosities studied at those temperatures should be proportional to their molecular weights in the liquid state.

The author proposes to show, how far his condition of equal free space agrees with that obtained from corresponding temperatures and, also, how nearly the boiling-points can be considered to be corresponding temperatures.

It is well known that while Van der Waals's generalisations regarding corresponding temperatures, pressures and volumes are verified in a general way by actual liquids, they cannot be held to be strictly true except perhaps for a few closely allied substances. If we take an homologous series such as pentane, hexane, heptane, octane at some corresponding pressure, then, both the corresponding temperatures and volumes show a change of ratio with change of molecular weight.

Boiling-points are unsatisfactory temperatures at which to compare the viscosities of liquids. By correcting the boiling-points to a condition of equal free space, the viscosities of liquids become proportional to their molecular weights in the liquid state. Such a condition of equal free space corresponds very closely to a reduced temperature on the basis of Van der Waals's equation of state.

NEW DESIGN FOR APPARATUS TO MEASURE THE COEFFICIENT OF DEVIATION FROM BOYLE'S LAW; AND THE DETERMINATION OF THIS COEFFICIENT FOR ACETYLENE.

By J. T. HOWARTH and F. P. BURT.

The pressure of the imprisoned gas was found in terms of the height of a column of mercury supported by the gas, as measured by a glass scale, graduated in millimetres, and a telescope provided with a micrometer eyepiece. The volume of the gas could be altered at will by the withdrawal of weighed quantities of mercury from the containing vessel. This vessel was connected with the manometer by capillary tubing expanding into a small, calibrated, point-carrying dead-space which constituted the lower chamber of the manometer. While the main bulk of the gas was kept at 0° C., the dead-space and manometer were enclosed in a water-bath at room temperature.

The accuracy with which a mercury meniscus can be set to a glass point (setting being adjusted with a pocket-lens) is very much greater than that with which the position of a meniscus referred to a scale can be read with a telescope. Improvements in results should therefore be obtained by replacing the scale by a series of points sealed into the manometer tube at different levels, provided that the vertical distances of these points above the dead-space point could be determined once for all with sufficient exactitude.

The essential features of the new apparatus closely resemble the earlier apparatus, but the upper chamber of the manometer was furnished with six glass points, sealed to the bottom of the upper chamber and the top of the dead-space.

The minimum values of both pressure and volume should be measurable with an accuracy approaching 1 part in 10,000, so that the maximum error on the pv product should be of the same order. The diameter of dead-space and manometer tubing was 14 mm. and the height of the meniscus was found to be sensibly constant, so that capillarity errors must have been very small.

Since the volume of gas at atmospheric pressure was only about 8 c.c., variation of a few c.mm. in the amount of gas taken up by the glass walls between the experimental pressure limits would affect the coefficient seriously. From independent observations it was estimated that the total quantity of acetylene taken up by the walls of the volumeter at atmospheric pressure would not exceed 0·004 c.c., and that the variation (which alone could affect the results), would be only a small fraction of this. A direct test was made in the course of the measurements in the following manner. After a setting had been obtained at

a pressure of 388 mm., mercury was run out of the volumeter until the pressure was reduced to 105 mm., and the system left for several days at this pressure. Mercury was then introduced again right up to the mark (B) on the capillary, and from there weighed out until the original setting had been recovered. No detectable difference was found in the volume, the weights of mercury withdrawn agreeing to within 2 mgm. Since sorption by the fresh glass surface exposed would have greatly exceeded desorption from the overlying surface due to diminished pressure, and since, further, this latter effect would have been largely reversed on raising the pressure again, the absence of any significant change in the volume of gas measured, indicates that sorption variation was negligible.

ROYAL INSTITUTION.

The Before-Easter Lecture Arrangements at the Royal Institution have just been issued. The Subject of the Christmas Course of Lectures for Juveniles is "Concerning the Habits of Insects," to be delivered by Mr. F. Balfour Browne beginning on Dec. 27 on Insect Collecting, followed by the Habits of Bees and Wasps (Dec. 30), Caterpillars (Jan. 1), the Dragonfly (Jan. 3), the Water Beetle (Jan. 6) and the Habits of Insects and the Work of Man (Jan. 8). The General Courses will begin on Tuesday afternoon, Jan. 13, at 5.15, when Professor A. Fowler will commence a course of two lectures on the Analysis of Spectra; on succeeding Tuesdays there will be two lectures by Dr. H. R. Hall on the Prehistoric Greek and Ancient Egyptian Civilisations, four by Prof. Barcroft on the Colour of the Animal Creation, two by Prof. E. N. da C. Andrade on the Evolution of the Scientific Instrument, and two by Prof. A. S. Eddington on the Internal Constitution of the Stars. Thursday afternoons, at the same hour, beginning on Jan. 15, Mr. J. S. Huxley will give two lectures on the Courtship of Animals, and its Biological Bearings; Sir William Bragg, four on the Properties and Structure of Quartz; Sir A. Smith Woodward, two on Dinosaurs; Dr. Leonard Hill, two on the Biological Action of Light, and Mr. T. Thorne Baker, two on Chemical and Physical Effects of Light. The Saturday lectures will commence at 3 o'clock on Jan. 17, when Prof. G. Gordon begins a course of two lectures on (I) The Women of Shakespeare, (II) Shakespeare and the Spirit of Comedy, to be followed by two lectures by Canon E. H. Fellowes on (I) The Elizabethan Madrigal, (II) The Elizabethan Ayre, with musical illustrations; two by Mr. W. Rothenstein on the Artist's Relation to Social and Religious Life; four by Sir Ernest Rutherford on Counting of the Atoms, and two by Prof. J. H. Ashworth on a Zoological subject to be announced later. The Friday Evening Meetings begin on January 16 with a Discourse by Sir William Bragg on the Investigation of the Properties of Thin Films by Means of X-Rays. Succeeding Discourses will probably be given by Dr. A. W. Crossley, Professors J. W. Gregory, R. W. Chambers, T. H. Pear, Gilbert Murray, J. W. McBain, Principal Irvine, Mr. W. B. Hardy, Sir Ernest Rutherford, Sir Daniel Hall and other gentlemen.

SOCIETY OF PUBLIC ANALYSTS.
ORDINARY MEETING.

Held at the Chemical Society's Rooms, Burlington House, on 3rd December, 1924.

Mr. G. Rudd Thompson, President, in the Chair.

A Certificate was read for the first time in favour of Mr. Thomas Mann.

Certificates were read for the second time in favour of Messrs. Arthur Chapman Barnes, B.Sc., F.I.C., John Jacob Fox, D.Sc. (Lond.), F.I.C., Thomas Congalton Hay, Harold Rupert Jensen, M.Sc. (Liv.), A.I.C.

The following were elected Members of the Society: Messrs. Arthur Cecil Brooks, A.R.C.Sc.I., A.I.C., William Donovan, M.Sc. (New Zealand), Albert George Flower, B.Sc. (Lond.), Clifford Hollingsworth, F.I.C., George Marshall Norman, B.Sc. (Lond.), A.R.C.S., F.I.C., Charles Edward Sage, F.I.C., Percy Frank Spendlove, B.Sc., A.R.C.S., F.I.C., Charles William Spiers, M.Sc. (Bristol), A.I.C., Leslie Herbert Trace, A.I.C., B.Sc. (Lond.), James Rawson Walmsley, A.M.S.T., F.I.C.

The following papers were read:—

"The Analytical Value of the Melting Point of the Insoluble Volatile Acids from Fats," by G. Van B. Gilmour, B.Sc., A.I.C., A.R.C.Sc.I.

The method put forward by Blichfeldt for distinguishing between and estimating coconut and palm kernel fats in mixtures

is investigated. It is found that the method has considerable limitations especially when there is a preponderance of other fats present. The melting points of the insoluble volatile acids from a number of edible oils and fats are given and it is shown that as little as 1 per cent. contamination with coconut or palm kernel fat can be detected by the lowering of the melting point. The volatility of oleic acid in ordinary distillations is demonstrated.

"The Use of Mitchell's Ferrous Tartrate Reagent in Qualitative Analysis," by A. H. Ware.

The author describes and discusses results obtained by the use of Mitchell's reagent with plant extractives in the presence and absence of alkalies, including a new modification of the test in which acetic acid is used. He finds the test in its different variations to be of very great value in plant analysis and pharmacognosy. A list is given of a considerable number of phenolic bodies of different classes, including catechol-bodies, giving in plant extractives a good violet colour-reaction to the test, in the presence of definite amounts of alkali; also of catechol-bodies which, although they resemble those of the first list in giving good green colour reactions with ferric alum, yield no violet colour to the test under discussion. The test affords a useful means of distinguishing between ipecacuanha extractives and a uumber of other extractives yielding a green colour to ferric alum, but which, like ipecacuanha, do not contain tannin. The modification of the test given by boiling with dilute acetic acid after adding the iron reagent, affords a very valuable means of distinguishing between two classes of gallic acid tannins. Those of one class give a good blue or violet colour reaction under the conditions named, whilst those of the other class do not show this result. The author gives a list of drugs and tanning materials, falling into the two classes referred to, and proposes that the term "gallotannins" should be confined to tannins which give the blue or violet coloration to the acetic acid modification of Mitchell's test.

"The Influence of Hydrogen Ion Concentration on the Colorimetric Estimation of Pyrogallol and Catechol Derivatives," by S. Glasstone, M.Sc., Ph.D., F.I.C.

The maximum intensity of coloration with Mitchell's ferrous tartrate reagent is obtained within the limits of PH 6·5 and 10·3 for pyrogallol, 5·9 and 10·3 for gallic acid, and 4·1 and 11·1 for gallo-tannin. Hence the conditions described by Mitchell are suitable for obtaining equal intensities of the violet colour. In the case of catechol derivatives, however, the limits are much narrower and suitable adjustments of the PH value are necessary to obtain quantitative results. The author recommends the addition of ammonium acetate, to act as a buffer and to give a PH value of about 7·6.

"The Futility of Sealing: A Suggestion for its Safeguarding," by B. S. Evans, M.B.E., M.C., B.Sc., F.I.C.

The suggestion is made that plain wax seals should be used on which the person sealing should write his initials in special ink. A number of these inks should be kept, consisting of ordinary ink holding in solution substances easily identifiable in minute traces. The person breaking the seal would, after identifying the signature, dissolve it off the wax and test the solution for the key substance of which he would be privately notified.

New Patents.

This list is specially compiled for "Chemical News" by Rayner & Co., Regd. Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

Latest Patent Applications.

28349.—Badische, Anilin & Soda Fahrik.—Manufacture of carbonyl compounds. Nov. 26th.

28138.—Lomax, E. L.—Methods of separating phenols. Nov. 24th.

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THE ALEXANDRIAN SCHOOL.

By J. G. F. DRUCE, M.Sc. (Lond.), R.Nat.Dr. (Prague).

(Continued from Last Week.)

Astronomy.—By comparing the height of the sun at its zenith simultaneously at Cyrene and Alexandria, he determined the difference of their latitudes and hence was able to give the first scientific estimate of the earth's size. His results were surprisingly accurate considering the poor quality of the instruments at his disposal.

With regard to the study of astronomy, Aristarchus (born about B.C. 270) wrote a treatise on the dimensions and distances of the sun and moon, in which may be traced an anticipation of Copernicus. He understood that the alternation of day and night was caused by the earth rotating on its axis.

Hipparchus, another astronomer (about B.C. 140), compiled a list of the known stars, totalling over 1,000. He appears to have been a particularly good teacher. The precession of the equinoxes was discovered at this time, but the results and calculations were very rough since trigonometry was unknown, although Hipparchus himself laid the foundations of that branch of mathematical science.

Time was still generally measured by the flow of water, although the Greeks must have seen the Egyptian shadow-clocks.

After the time of Hipparchus no noteworthy progress was made until Claudius Ptolemy (about A.D. 100) introduced the Ptolemaic System. This system supposed, as did the early Greeks, that the earth was the centre of the universe.

By this time the Alexandrine astronomers had traced the sun's apparent yearly path through the heavens. They divided this path into twelve parts and called each after a cluster of stars (or constellation). These clusters of stars were known by the names of animals and were termed the Zodiac. They are: 1, Aries—the Ram, 2, Taurns—the Bull; 3, Gemini—the Twins; 4, Cancer—the Crab; 5, Leo—the Lion; 6, Virgo—the Virgin; 7, Libra—the Balance; 8, Scorpio—the Scorpion; 9, Sagittarius—the Archer; 10, Capricornus—the Goat; 11, Aquarius—the Water Bearer; 12, Pisces—the Fishes.

It was by no means an easy thing to trace the sun's path among the stars, because the sun and the stars are never in sight at the same times, so astronomers were obliged to notice the constellations as they appeared close to the sun after it set at night or before it rose in the morning. These, they found, varied a little each night, till, when a whole year had passed away, each of the twelve signs had been in turn close to the sun, and the cycle began again. Thus they learned that the sun passed over each of the twelve signs in the course of the year; and they thought from this that the sun travelled round the sky while the earth stood still in the middle.

Mathematics.—The demands of astronomy first led to the intensive study of mathematics, and by means of trigonometry the earliest mathematical tables were compiled.

During the period of its decline Pappus and Diophantns were two Greek mathematicians at Alexandria about A.D. 300. Pappus wrote a volume collecting the mathematical knowledge of the time, including the trigonometry as then worked out, and some optics. It was Diophantus who wrote one of the earliest treatises on Algebra, using symbols in place of words. His "Arithmetic" is really a work on algebra since numerals were not used then. He was able to solve quadratic equations, and certain problems in alpebra are still called *Diophantive problems*.

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CHEMICAL NEWS, MERTON HOUSE, SALISBURY SQUARE, LONDON, E.C.4.

Under the Romans, the brilliant work of these two men excited no interest. Mathematics no longer attracted the intellects of the day. Progress in science slackened and the discoveries were made elsewhere.

Medicine.—The School at Alexandria included men who studied medicine and anatomy, probably as an outcome of the embalming practices of the Egyptians. Herophilus (about B.C. 300) began a study of several organs of the body such as the brain and the liver. Another anatomist, Erasistratus, examined and described the heart, brain and nerves at about the same time. This was a great step forward, for previously little progress was possible because Egyptian doctors had confined their attention each to one organ.

In connection with early biology, the fleets of the Ptolemies made regular trade voyages to Arabia and tropical Africa. By this means elephants, rhinoceroses, buffaloes, monkeys, ostriches and other animals were brought to Alexandria. Many were afterwards kept in a menagerie there.

A feature of the work at the School or Museum of Alexandria was the copying of books. Thus began the supplying of "editions" of important works. It should be borne in mind that these "books" were rolls, which had to be tediously wound backwards and forwards in order to refer to any particular passage.

THE BROMINATION OF SUBSTANCES CONTAINING A THIAZOLE RING PART IV.: THE STRUCTURE OF THE BENZOTHIAZOLE BROMIDES AND THE HUGERSHOFF SYNTHESIS OF THE BENZOTHIAZOLE BROMIDES FROM ARYLATED THIO UREAS AS APPLIED TO 1 PHENYLAMINO BENZOTHIAZOLE TETRABROMIDE.

By R. F. Hunter, B.Sc., A.R.C.S., F.C.S., M.S.Chim.

In the papers which have already been published on the subject of the benzothiazole bromides (*The Chemical News*, 1923, CXXVII., 325, *The Chemical News*, 1924, CXXVIII., 147, CXXIX., 125 and 235) by the author, the view has been expressed that the bromination of substituted benzothiazoles of the type of dehydrothiotoluidine to give dibromo addition products is due to the fission of the double bond (1:2) of the fused thiazole nucleus, with the consequent addition of two bromine atoms at this position in the case of dehydrothiotoluidine to form 4′ amino 1 phenyl 5 methyl benzothiazole 1:2 dibromide. The ready formation of the brom addition products by the substituted benzothiazoles, the generality of the reaction and in some cases the relative instability of the addition products is in agreement with this view.

The main objection to the mechanism which has already been pointed out by the author (loc. cit) is the fact that on the basis of the hypothesis outlined above, the bromine addition products are formulated as having a bromine atom directly linked to a nitrogen atom, a configuration which in the case of inorganic compounds such as nitrogen tribromide is an exceedingly unstable one, whilst the benzothiazole bromides are in many cases crystalline compounds of definite melting point and quite lacking in explosive properties such as might reasonably be looked for on the formulation of 1:2 dibromides. It is of course true that the comparison of, say, dehydrothiotoluidine dibromide with nitrogen tribromide is scarcely a fair one, for in the case of the inorganic compound, each nitrogen valency is directly linked to a bromine atom, whilst in the case of the brom thiazole only one valency in the formulation postulated in this series of papers, is directly linked to a bromine atom, whilst the other two nitrogen valencies participate in a stable five membered heterocyclic ring jointed to a six membered homocyclic benzenoid ring by two carbon atoms common to both. The instability induced by the direct attachment of bromine to nitrogen in the case of the brom thiazole must be looked upon as being of a lesser magnitude than the direct linkage of bromine to a nitrogen atom whose other two valencies likewise carry bromine atoms, since the former nitrogen is included in a stable ring system.

Again, the view that bromine addition is due to the fission of the double nitrogen carbon linkage of the fused heterocyclic ring, although accounting for the formation of dibromo addition products of the type of dehydrothiotoluidine dibromide, acetyldehydrothiotoluidine dibromide and the dibromides of the dehydrothioxylidines (*Berichte* 1889, XXII., 422, 580, *The Chemical News* 1924, CXXIX., 125) does not account for the formation of 1 phenyl benzothiazole tetrabro-

mide by the bromination of a glacial acetic acid solution of 1 phenyl benzothiazole (*Jour. Amer. Chem. Soc.* 1922, XLIV., 826), although the explanation of this might lie in the occurrence of a tautomeric form of the thiazole more unsaturated than the normal form and in equilibrium with the latter in solutions of phenyl benzothiazole.

It has already been pointed out (*The Chemical News* 1924, CXXIX., 237) with regards 1 phenyl benzothiazole tetrabromide, that there exists a choice of two structures for the compounds, namely the formulation as 1 phenyl benzothiazole 1:2:7:7 tetrabromide (I) or as 1 phenyl benzothiazole 2:2:7:7 tetrabromide (II).

$$C_6H_4 < \begin{matrix} SBr_2 \\ NBr \end{matrix} > CBr\ C_6H_5$$

(I)

$$C_6H_4 < \begin{matrix} NBr_2 \\ SBr_2 \end{matrix} \geq CC_6H_5$$

(II)

The formulation (I) contains a trivalent nitrogen atom directly linked to a bromine atom, and therefore represents an unstable system, which might reasonably be expected to exhibit in a certain degree explosive properties, whilst phenyl benzothiazole tetrabromide (this vol., 240) is a crystalline substance of definite melting point and quite devoid of explosive tendencies. The formula (II), on the other hand, represents a compound of the perbromide type containing two bromine atoms directly linked to a pentavalent nitrogen atom, a configuration which is quite different from the one containing trivalent nitrogen, since organic compounds possessing a pentavalent nitrogen atom which is directly linked to a halogen or to halogen atoms are well known to be quite devoid of explosive properties and of a relatively stable nature (this vol. 247). From this it is clear that the formula (II) is best in accordance with the experimental data. The similar conversion of the divalent ring sulphur atom into the tetravalent state by the direct addition of two bromine atoms calls for no comment. The view that brom addition in the benzothiazoles does not consist of the fission of the double bond (1:2) of the fused thiazole ring but consists of the direct addition of two bromine atoms at the position (2) with the conversion of the ring nitrogen atom into the pentavalent state receives additional support from the existence of benzothiazole methiodides analogous to the methiodides of the pyridine series.

Another question which receives adequate explanation from the view that the brom benzothiazoles have the structure (II) is the reduction of the compounds by sulphurous acid to the original bases, the bromine being eliminated as hydrobromic acid. This reduction and elimination of halogen is in accordance with the configuration of something in the nature of a perbromide, and is therefore in accordance with the formula (II).

The discovery of the existence of 1 phenyl-benzothiazole di iodide by Bogert and Abrahamson (*Jour. Amer. Chem. Soc.* 1922, XLIV., 826) is a proof of the fact that this halogen addition of the benzothiazoles is not confined solely to bromine, and that the fused thiazole ring is capable of adding iodine atoms in a manner similar to its addition of bromine atoms which has been shown to be general with regards all the substituted benzothiazoles so far examined by the author (loc. cit).

As well as furnishing fascinating examples of what we might term the unsaturated nature of the bicyclic benzothiazole system, the bromine addition products of the benzothiazoles have an additional interest, namely the part which they play in the synthesis of the benzothiazole ring system by the bromination of chloroform solutions of the arylated thio ureas, in other words, the interest which they derive from the Hugershoff synthesis (*Berichte* 1903, XXXVI., 3121) of 1 arylamino benzothiazoles.

The halogenation of the thio ureas has been investigated by many investigators, notably Otto (*Berichte* 1869, II., 409), Hofmann (*Berichte* 1869, II., 453), Belstein and Kurbatow (*Berichte* 1874, VII., 235). Mac Gowan (*Jour. fur. prakt Chem.*, 1886, 33, 188) and Hugershoff (*Berichte* 1901, XXXIV., 3130), and it will be recalled that in his investigation, Hugershoff chose a solvent inert towards both the thio ureas and bromine, namely chloroform, with the object of eliminating secondary reactions. By the bromination of phenylthiourea in chloroform solution, Hugershoff obtained what he believed to be the tetrabromide of carbaminophenyl iminodisulphide

which passed on reduction with sulphurous acid into carbaminophenyliminodisulphide, the HBr salt of which on bromination in chloroform suspension gave the same compound as was obtained by the bromination of phenylthiourea in the same solvent. At a more later date, however (*Berichte* 1903, XXXVI., 3121), Hugershoff found that the so-called carbaminophenyliminodisulphide had not the properties of a disulphide, its sulphur atom being quite unaffected by reducing agents such as sodium amalgam, tin and hydrochloric acid, and the compound in fact exhibiting stability which was far from being in accordance with the formula for carbaminophenyliminodisulphide. Hugershoff further discovered that the so-called carbaminophenyliminodisulphide was identical with 1 amino benzothiazole previously prepared by Hofmann by the action of ammonia on 1 chlorobenzothiazole obtained by treating phenyl isothiocyanate with pentachloride of phosphorus (*Berichte* 1879, XII., 1129 and 1880, XIII., 11). Similarly diphenylthiourea on bromination in chloroform solution, followed by reduction of the bromo product, was found to give 1 anilidobenzothiazole previously characterised by Hofmann (*Berichte* 1880, XIII., 11) and Jacobson and Frankenbacher (*Berichte* 1891, XXIV., 1410). Following this, Hugershoff brominated di o tolylthiourea and di p tolylthiourea and prepared 1 o tolylamino 3 methylbenzothiazole and 1 p tolyamino 5 methyl benzothiazole.

The study of the bromination of various arylate dthio ureas and related compounds is at present being carried out in this laboratory with the object of synthesising new benzothiazoles of a more complex type, the results of which it is hoped to be able to publish shortly. For this reason, the reaction by which Hugershoff obtained 1 anilidobenzothiazole by the bromination of diphenylthiourea has been subjected to a very close study. The mechanism of the synthesis appears at first sight to be as suggested by Hugershoff in his second paper (*Berichte* 1903, XXXVI., 3121) and to consist of the formation first of a yellow addition product of the thio urea formed presumably by the fission of the double sulphur carbon linkage in diphenylthiourea with addition of two bromine atoms at the thiocarbonyl grouping, followed by ortho ring substitution and thiazole ring formation elimination of two molecules of hydrobromic acid, the benzothiazole being isolated at its brom addition product. This mechanism, however, from the present author's point of view, is only an approximation to the truth, for it does not adequately explain the fact that the thiazole is always necessarily obtained as its brom addition product.

When diphenylthiourea is brominated in chloroform suspension as described in the experimental part of this paper, the first product isolated consists of bright tile red crystals of 1 anilido benzothiazole bromide which melt about 115° C. and readily decompose at 120° C., these red crystals on keeping in air or in a non-evacuated dessicator undergo change, falling to a bright yellow crystalline powder which melts some ten degrees higher or so than the original red compound and whose production entails the partial elimination of bromine from the tile red crystals, this compound after keeping for several days appears to be quite stable and no longer smells of bromine to any appreciable extent. Puzzling results have been obtained by the author with these compounds with regards the determination of halogen by the method of Piria and Schiff, the bright red compound giving figures about 6 per cent. low with regards bromine calculated or tetrabromide even after having been transferred immediately after its formation to an evacuated dessicator previously tested for leaks and being kept in such a vaccum over pure solid potash for no more than two hours previous to analysis. Hugershoff, it will be recalled, records a tetrabromide melting at 136°, so far the author has not been able to obtain any brom addition product melting at this temperature, the yellow crystalline compound which is obtained on exposing the red crystallisation of a specimen from warm chloroform gave bright yellow crystals melting some twenty degrees above the original melting point. Hugershoff states that a dibromo substitution product of 1 anilidobenzothiazole is obtained in recrystallising the bromide from alcohol, since the bromide is converted nto the substitution product by treatment with warm alkali for a few minutes, this is not remarkable in view of the hydroxylic nature of alcohol as a solvent, but such a thing is of course impossible with chloroform and the recrystallised compound from chloroform would appear to be nothing more than the purified compound, since in appearance, colour etc., it is the same as the uncrystallised material. The matter is in any case at present being

investigated by the author at the Royal College of Science, and it is hoped to furnish an adequate explanation of these rather peculiar facts at a later date.

Diphenylthiourea was brominated in chloroform suspensions and solutions as described by Hugershoff, the red crystalline compound melting at 115° to 120° isolated which was converted into the yellow crystalline bromide on exposure to air as recorded commencing to melt usually in the region of 125° and with decomposition at 130°. The bromides were also reduced by sulphurous acid as recorded, an attempt was made to estimate the elimination of bromine by a Fischer Volhard titration with several specimens, the excess of sulphurous acid being destroyed by means of hydrogen peroxide, excess silver nitrate being added and the excess titrated in the presence of ferric indicator. Accurate results could not be obtained owing to the rapid discharge of colour of the indicator and the tendency of the thiazole to resinify during reduction. The results of halogen analysis by means of the Piria and Schiff method have been peculiar as already intimated. With regards the reduction of the brom thiazoles, it is hoped to discuss the question more fully in a later paper on the formation and stability of the brom benzo thiazoles.

EXPERIMENTAL.

Diphenylthiourea.—In the earlier experiments this was worked up from aniline, alcohol and carbon disulphide following the directions of Gatterman. At a later date, the 100% thiocarbanilide of the B.D.C. was purchased and used after recrystallisation from alcohol.

The Bromination of Diphenylthiourea in Chloroform.—10 gms. of diphenylthiourea were introduced into 50 ccs. of redistilled chloroform in a 500 cc. round bottomed flask, the suspension gently warmed and cooled. 8 ccs. of bromine were dissolved in an equal volume of chloroform and slowly added with shaking to the suspension in the flask. A yellow brom addition product of the thio urea first separated and then redissolved with evolution of heat and hydrogen bromide on further addition of halogen. On complete addition a warm clear red solution was obtained, which evolved hydrogen bromide from time to time. The flask was allowed to stand for a short time and then attached to a condenser and heated on a boiling water bath for twenty minutes or more. During the process of refluxing a copious evolution of hydrogen bromide took place at the top of the condenser and red crystals of the bromide were filtered and the filtrate transferred to a distilling flask and concentrated on a water bath. On cooling and shaking the bottom of the flask became nearly solid with tile red crystals, which were filtered, readily dried on a porous plate transferred to a clock glass in a vacuum dessicator over fresh solid potassium hydroxide. The dessicator was evacuated and the crystals kept in the vacuum till required.

The Tile Red Crystals: so obtained melted at 115°. On exposure to air they fell to a yellow crystalline powder, which was relatively stable.

The Yellow crystals: formed by partial elimination of bromine from the tile red crystals melted at 125° and decomposed at 130°.

1 Anilido benzothiazole: Both bromides on reduction with sulphurous acid, followed by treatment with sodium hydroxide, gave 1 anilido benzothiazole.

Brom substitution product of anilidobenzothiazole: This was obtained either by treating anilidobenzothiazole bromide with water or with 10% sodium hydroxide.

With regards the bromination of arylated thio ureas, it is desired to state that an analogous series of experiments are being carried out with various arylated thio ureas using carbon tetrachloride as a medium for bromination. Carbon tetrachloride should resemble chloroform in its inertness to both bromine and the thio ureas, and hence the products of bromination would be expected to be thiazole bromides. The influence of the solvent on the bromination on thio ureas is of course a very important factor, for it will be recalled that phenyl thio urea, while it brominates in chloroform solution to give 1 amino benzothiazole bromide, brominates in ethyl alcohol to give a derivative of tetrahydro 1:2:4 thiodiazole, similarly diphenylthiourea when brominated in ethyl alcohol yields 2:4 diphenyl 3:5 diphenylimino tetrahydro 1:2:4 thiodiazole.

The Chemical Laboratory,
Highbury New Park,
N.5.

October, 1924.

General Notes.

RESEARCH AND THE AGRICULTURAL INDUSTRY.

On December 12th, the Minister of Agriculture (Mr. Edward Wood) laid stress on the importance of maintaining, if not increasing, arable cultivation. It was not too much to hope that Wales might achieve a somewhat higher measure of productivity than it had reached to-day. They had a large quantity of grass-land, and it would differ from all other grass-lands in the world if it could be made, by judicious treatment, to carry a somewhat larger head of stock. He had been told by a scientific friend that, broadly speaking, all the land to the west of a line drawn down the centre of the map of England was deficient in lime. This, if true, suggested one direction in which greater productivity might be sought.

Research Work.

After giving an outline of pending legislation, the Minister went on to say that there was nothing more important than the encouragement of scientific research, and he intended, while he was at the Ministry, to follow the excellent example of his predecessors in pressing for more money to push the question of research and scientific development and education. He did not feel quite satisfied that all the results of the scientific work done in the laboratories was getting out and down to the ordinary working farmer. They had not succeeded in establishing a good liaison between the scientific side and the men who had to apply them on the farm. He wanted to see if something could not be done to develop the business of demonstration on the farm, in order to make available to the farmer what science had to tell them.

On the subject of land drainage, Mr. Wood said about 300 schemes had been approved of and another 130 were under consideration. If all these were approved, the total cost would be about £400,000, of which the Government would find £300,000 —a very substantial contribution to a local activity of great importance.

MOTOR CARS IN URUGUAY.

Mr. Reid Brown, British Vice-Consul in Montevideo, calls attention in his Report, dated September last, to the striking increase in the imports of American motorcars. So far as general trade is concerned, Great Britain holds her own, though Germany continues to advance.

WHOLESALE PRICES IN NOVEMBER.

A reduction equal to about one-tenth of one per cent. is noted in the general level of wholesale prices for last month as compared with October, the Board of Trade Index Number being returned at 169.8, against 170. The figure for November, 1923, was 160.8

BRITISH INDIAN IMPORT TRADE.

Compared with the corresponding period of last year imports from the United Kingdom into British India during the first half of the current fiscal year rose from 65 to 67 crores of rupees in value, but fell from 59 to 54 per cent. in ratio to the total import trade.

TRADE AND INDUSTRY OF BRITISH COLUMBIA.

During the first nine months of this year trade, especially in hardware, logging and mining machinery, dry goods, groceries, and general lines, showed an improvement over the corresponding period of last year.

DIRECTION OF CHINESE TRADE.

Imports into China from Hong Kong, Singapore and British India were larger last year than in 1922, but those from Great Britain were smaller, although Germany, France, and Italy all exported more to China. In China's export trade Great Britain, British India, and several European countries had a larger share, but France and Russia took less.

ANGLO-GERMAN COMMERCIAL TREATY.

We give the text of the Anglo-German Commercial Treaty and Protocol which were signed in London on 2nd December. In the opposite column we publish a note on the duration of the Treaty.

SHIPPING MOVEMENTS AT BRITISH PORTS.

October figures of the foreign trade show decreases in tonnage arrived of 2.2 per cent. and in tonnage departed of 0.6 per cent., as compared with October, 1923, owing to the fall in coal exports. In the coasting trade increases of 5 and 1.3 per cent. were registered.

WEEDS OF SOUTH AFRICA.

The Editor of the *Journal of the Department of Agriculture,* Union of South Africa, says :

Like other countries, South Africa is awaking to the importance of suppressing its noxious weeds, which, owing to the alarming rapidity of their spread in recent years, are becoming increasingly dangerous to our pasturage, wool, and other agricultural pursuits. While much has been done in the past to place the farmer in a position to recognize and cope with the danger, the problem grows in seriousness, and the time has arrived when all information regarding the noxious weeds found in the Union should be gathered into one publication for the use of the farmer, the student, and the general public. This work has now been undertaken by the Division of Botany, the opening contribution, continued hereunder, appearing in our April, 1921, number. The publication, which includes an illustrated glossary on the morphology of weeds, is the first of its kind in South Africa, and will continue to appear in serial form in the *Journal.* Thereafter, the series will be reprinted in bulletin form, with the addition of a coloured plate illustrating each weed dealt with.

BRITISH COLUMBIA MINING NEWS.

The High Commissioner for Canada says that a review of the mining situation in British Columbia at the 1924 field season brings out the following facts : (1) Although some of the exploratory development work which looked promising last season has been disappointing, a number of interesting and significant discoveries have been made during the season. (2) A number of properties which have been closed for many years are being reopened and others are about to be opened. (3) There is a keen demand for mining properties, particularly gold, silver, lead and zinc, with considerable capital being spent in search of such properties, and a still larger amount available for any opportunities which may arise. (4) Placer gold mining is particularly active, and three discoveries have been reported. The Kafue Copper Development Company's dredge is about to commence operations in the Cariboo, and Cedar creek is still yielding surprisingly large amounts of coarse gold. (5) The established mines of the province have maintained a steady and, in some cases, an increased production so that this year's total output is likely to exceed that of last year by a large amount.

SOME DISCOVERIES.

(1) A small vein of zincblende, carrying from $200 to $500 to the ton in gold was found near the mouth of the Zaballos river which flows into the head of Esperanza inlet on the west coast of Vancouver island. The vein, so far as is yet known, is only a few inches wide and a few feet in length. (2) On Emory creek near Yale was found an outcrop 40 feet wide, 30 feet high and 100 feet long of nickel ore carrying 1.7 per cent. of nickel and a small amount of copper. (3) Mr. Ewen Morrison discovered on Vancouver Island a deposit of realgar (arsenic sulphide). Mr. Morrison reports that a zone 12 feet wide containing disseminated realgar and a small amount of native arsenic, and having series of lenses of solid realgar up to 2 feet in width scattered along the footwall has been traced on the surface for 350 feet. (4) What appears to be the most important discovery of the season was made on the Gold Cliff group of claims, $2\frac{1}{2}$ miles from the town of Stewart.

On this property which is under bond to A. B. Trites, of Vancouver, is a vein averaging five feet in width which has been traced for 1,200 feet and which runs as high as 9267 to the ton in lead, silver and gold. Two parallel veins have recently been discovered on the same property. (5) A body of very rich ore was discovered on the MacIntosh property in the Beaverdell district, from which several shipments were made.

METROPOLITAN-VICKERS ELECTRICAL COMPANY'S BIG CONTRACT.

The above Company of Trafford Park, Manchester, have secured the contract to supply the Switch Boards and Transformers for the new Wilhank Generating Station and Brakpan Distribution Station of the Victoria Falls and Transvaal Power Company, Limited. The value of the order is £250,000.

REMOVAL NOTICE.

We have been advised that Messrs Jas. Milne Cooper & Co., Ltd., have removed their Offices and Works to Kobar Works, Ambler Street, Bradford, England.

NATIONAL SAFETY FIRST ASSOCIATION,

119, Victoria Street, London S.W.

This Association has issued useful Leaflets on Fire and Accident Prevention, etc.

DYESTUFFS (IMPORT REGULATION) ACT, 1920.

Applications for Licences in November, 1924.

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during November has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee.

The total number of applications received during the month was 439, of which 335 were from merchants or importers. To these should be added 12 cases outstanding on the 1st November, making a total for the month of 451. These were dealt with as follows :—

Granted—304 (of which 273 were dealt with within 7 days of receipt).

Referred to British makers of similar products—89 (of which 77 were dealt with within 7 days of receipt).

Referred to Reparation Supplies available —23 (all dealt with within 2 days of receipt).

Outstanding on 29th November, 1924—35.

Of the total of 451 applications received, 373 or 83 per cent. were dealt with within 7 days of receipt.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE ROYAL SOCIETY.

Thursday, December 4, 1924, at 4.30 p.m.

PAPERS READ.

A Fowler, F.R.S.—The Structure of the Spectrum of Ionised Nitrogen.

H. Jeffreys.—On the Formation of Water Waves by Wind. Communicated by Prof. G. I. Taylor, F.R.S.

J. E. Jones.—(1) On the Determination of Molecular Fields. III—From Crystal Measurements and Kinetic Theory Data. Communicated by Prof. S. Chapman, F.R.S. (2) On the Atomic Fields of Helium and Neon. Communicated by Prof. S. Chapman, F.R.S.

F. S. Tritton.—A Centrifugal Method of Making Small Pots of Electrically Fused Refractory Materials. Communicated by Dr. W. Rosenhain, F.R.S.

PAPERS READ IN TITLE ONLY.

J. W. Nicholson, F.R.S.—Spheroidal Wave Functions.

J. V. Howard & S. L. Smith.—Recent Developments in Tensile Testing. Communicated by Prof. W. E. Dalby, F.R.S.

F. C. Harris.—The Photo-Elastic Constants of Glass as affected by High Temperatures and by Lapse of Time. Communicated by Prof. L. N. G. Filon, F.R.S.

A. L. Narayan & D. Gunnaiya.—Absorption and Dispersion of Thallium Vapour. Communicated by Lord Rayleigh, F.R.S.

R. d'E. Atkinson.—Note on Vegard's Theory of the Aurora. Communicated by Prof. F. A. Lindemann, F.R.S.

Mollie Weinberg.—The Spark Spectra of Indian and Gallium in the Extreme Ultraviolet Region. Communicated by Prof. J. C. McLennan, F.R.S.

S. W. Richardson.—The General Law of Electrical Conduction in Dielectrics. Communicated by Sir William Bragg, F.R.S.

T. Lewis.—The Interpretation of tbe Results of Bucherer's Experiments on e/m. Communicated by Prof. G. A. Schott, F.R.S.

A. M. Mosharrafa.—On the Quantum Dynamics of Degenerate Systems. Communicated hy Prof. O. W. Richardson, F.R.S.

E. G. Dymond.—On the Precise Measurement of the Critical Potentials of Gases. Communicated by Sir Ernest Rutherford, F.R.S.

I. Langmuir & K. H. Kingdon.—Thermionic Effects caused by Vapours of Alkali Metals. Communicated by Sir Ernest Rutherford, F.R.S.

INSTITUTE OF PETROLEUM TECHNOLOGISTS.

THE OILFIELDS OF ARGENTINA.

By Campbell M. Hunter, O.B.E., M.A., A.M.Inst.C.E., F.G.S., F.R.G.S.

In the course of his Paper, Mr. Hunter says that scientific attention was first directed to the oil possibilities of Argentina about 1885, when Stelzner made a geological investigation of the oil occurrences on the western slopes of the Sierra de Uspallata, close to Agua Zorra, Cacheuta, in the Province of Mendoza. Examination of the sedimentary formations with which these occurrences of oil were associated proved them to be of Rhætic age. In the following year drilling operations were commenced at Cacheuta, by the Compania Mendocina de Petroleo, under the direction of Dr. Zuber, who in 1890 published his first monograph on the district.

From 1890 to 1900 great interest was shown in the discovery and study of various oil and bitumen occurrences in the Andean foothills extending southward from Mendoza as far as the Province of Neuquen. The first important discovery was that of asphalt at the mines Eloisa y Roca, situated in the valley of the River Manga, one of the tributaries of the Rio Atuel. At first this substance was confused with that of coal, but the investigations of Dr. Zuber of the oil seepages at Cerro los Buitres and Cerro Alquitran dispelled this error. The formations responsible for these seepages were assigned originally to Rhætic age, and it was not until Bondenbender concluded his survey of oil indications as far south as Neuquen that it was recognised the formations belonged to Tithonian age.

Between 1896 and 1903 much geological work was carried out by Burckhardt, in the Territories of Neuquen and Rio Negro, and the basis was laid of our present knowledge of the stratigraphy of the Jurassic and Cretaceous periods in the Argentine Cordillera.

Between 1905 and 1907 Ameghino, Wilckens and Haupt directed their attention to the geology and palæontology of various areas in this zone.

In 1908 and 1909 drilling operations were commenced in the Neuquen area at Cerro Loteña by the "Neuquen Oil Syndicate," also at Covunco by the "Acme Oil Syndicate." These operations proved abortive, mainly owing to transport difficulties, and were suspended before commercial results were obtained. About the same time an Argentine company, called "El Petroleo Argentina," was formed to undertake the development of the oilfields at Los Buitres and Cerro Alquitran, situated some 200 kilometres from the town of San Rafael. Unfortunately, this company located its wells where, according to the forecasts of Dr. Zuber, the chances of success were rather slender. In spite, however, of this disadvantage, oil of a heavy character was struck in several wells.

In 1909 drilling was resumed in the Cacheuta district by an English company, called the "Argentine Western Syndicate," which, in the following year, formed the "Cacheuta Oil Syndicate." Several wells were drilled by the new company, but, again, the production was not found suffi-

ciently well maintained to make the venture a commercial success.

In Palæozoic times the present continent of South America formed part of the Brazil—Ethiopian Continent, Gondwana, which extended from South America to Africa. According to Dr. Windhausen, the western side of this old Continent was flanked by a great geosyncline, which in Tertiary times gave rise to the present Andean range. The Jurassic and Cretaceous sediments of this syncline are found extending in a great fan over Argentina, commencing in the north in the region of the Rio de los Patos, to the north of Aconcagua, and extending southward to Tierra del Fuego. The history of this geosyncline in Jurrassic and Cretaceous times was associated with numerous oscillations along the coast-line, transgressions and regressions following each other in frequent succession. On the base of the porphyrites and granites of probably Palæozoic and Triassic age are found the conglomerates of the Triassic transgressions, followed upwards by Lias and Dogger sediments, whose faunal contents bear considerable resemblance to corresponding European types. A new transgression began in Kimmeridge-Tithonian times, the tendency towards the deepening of the geosyncline continuing until the middle of the Cretaceous epoch. The most remarkable phenomenon of this second marine transgression is the faunal and petrographic uniformity which is rarely equalled elsewhere. Thus, the Kimmeridge and Tithonian beds are found in Neuquen with the same characteristics as in the region of Aconcagua, these beds as well as the Neocomian being specially characterised by great abundance of types, species and individuals. As in other parts of the world, the marine fauna attained during this epoch the height of its development in the Sub-Andean period. Above the Neoconian marine deposits lie the "Variegated Sandstone series" which here represent the Upper Cretaceous. These sandstones correspond with periods of regression of the sea towards the Pacific and represent a period of mainly continental conditions. Towards the end of this period the orogenetic movements commenced during which the great Andean fold along the coast of the Brazil-Ethiopian Continent was formed.

Such, in broad outline, is the history of the Andean Mesozoic geosyncline, which subsequently was subjected to tectonic movements.

ROYAL INSTITUTION.

21, Albemarle Street, London, W.

Lecture by F Balfour Browne, M.A. (*Lecturer on Entomology, Cambridge*).

Saturday. December 27, 1924.

Insect Collecting and what it Leads to.

It depends mainly upon the collector whether his collections are worth anything to himself or to anyone else. He may start without any clear idea as to his aim, but sooner or later, consciously or unconsciously, he will settle down to some particular line of work, and we may consider three such lines. The naming of insects is the first, since masses of un-named and untidily arranged insects are of little interest to anyone. We shall consider very shortly the kinds of characters upon which insects are divided into groups and species. A second line of work is the noting and mapping of the places in which different insects are found. Thus, some insects are found in most parts of a country, others only in the north or south, or in certain districts. Some are confined to woodlands, others to marshes, and so on, and such discoveries lead us to consider why insects are thus distributed, and thus we see that collecting may lead us to a study of geographical distribution and all its fascinating problems.

Tuesday, December 30, 1924.

The Habits of Bees and Wasps.

The third line of work arising out of collecting is the study of the life history and habits of insects. Attempts in this direction call forth cleverness and patience on the part of the enquirer, but the work is not difficult, and, by its interest, well repays the time it takes. How it can be done will be explained by referring to definite life histories which have been followed out, and, in this lecture, the work upon certain bees and wasps will be outlined. These are not the ordinary bees and wasps which live in large families and which are called "social" forms, but kinds which work each

one for itself, and which have consequently been called "solitary" species.

These kinds can be attracted to gardens if they are provided with suitable nesting places, and this lecture will explain how this can be done.

Thursday, January 1, 1925.

THE HABITS OF CATERPILLARS.

Caterpillars, except that they differ in colour and hairiness, may seem to be of little interest to the casual observer, but one has only to investigate a little into their domestic affairs to discover that many of their habits are most entertaining. Most caterpillars spin silk, and we can, in this lecture, investigate the uses made of silk, not by human beings, but by the insects which produce it.

We find that this habit of producing and making use of the silk has developed, in some caterpillars, a family life by which the brothers and sisters live together in silken webs, in the construction of which they all assist; and we can trace this habit from the very simple web, only used while the caterpillars are very young, to a strong shelter, which forms the home for the whole family for most of its growing stage, and from which the caterpillars go out to feed and to which they return to rest and sleep.

(To be Continued).

INSTITUTION OF ELECTRICAL ENGINEERS.

"Automatic and Semi-Automatic Mercury-Vapour Rectifier Substations." By G. ROGERS.

The paper briefly discussed the principal features of the mercury-vapour rectifier, and described a number of novel and successful applications of the use of automatic and semi-automatic mercury-vapour rectifier substations, designed for developing an efficient and economical direct-current supply to areas remote from existing sources of supply.

A method was given for feeding into an existing low-tension direct-current network by means of automatically controlled rectifiers for the purpose of improving the voltage and assisting already overloaded feeders.

THE ANNUAL EXHIBITION OF THE PHYSICAL SOCIETY OF LONDON AND THE OPTICAL SOCIETY.

This Exhibition, which is to be held on Wednesday and Thursday, January 7th and 8th, 1925, at the Imperial College of Science and Technology, Imperial Institute Road, South Kensington, will be open in the afternoon (from 3 to 6 p.m.) and in the evening (from 7 to 10 p.m.).

Mr. F. Twyman, F.R.S., will give a lecture on "Some Experiments with Interferometers," at 4 p.m. on January 7th and at 8 p.m. on January 8th. Mr. C. F. Elwell, B.A., M.I.E.E., will give a lecture on "Talking Motion Pictures" at 8 p.m., on January 7th and at 4 p.m. on January 8th. These lectures will include demonstrations. More than 50 firms are exhibiting scientific apparatus, and a number of experimental demonstrations have been arranged.

We understand that invitations have been given to the Institution of Electrical Engineers, the Institution of Mechanical Engineers, the Chemical Society, the Radio Society of Great Britain, the Rontgen Society, and the Faraday Society. Admission in all cases will be by ticket only, and Members of the Societies just mentioned should apply to the Secretary of the Society to which they belong. Others interested should apply direct to Prof. A. O. Rankine, Hon. Secretary of the Physical Society, Imperial College of Science and Technology, South Kensington, S.W.7.

PHYSICAL SOCIETY OF LONDON.

The Society met on November 28, 1924, at the Imperial College of Science, South Kensington, S.W.7.

A Discussion, arranged jointly with the ROYAL METEOROLOGICAL SOCIETY, was held on the subject of :—

"Ionization in the Atmosphere, and its Influence on the Propagation of Wireless Signals."

Chairman : F. E. SMITH, C.B.E., F.R.S.

PROGRAMME.

1. Opening Address. By Dr. W. H. ECCLES, F.R.S.

*2. "Atmospherical Ionization and its Variations." By Dr. C. CHERE, F.R.S.

*3. "Experimental Observations of the Strength of Wireless Signals as affected by the Path of the Signals, Time of Day and Season of Year." By Prof. E. V. APPLETON, M. A., DSc.

*4. "Atmospherics," By Mr. R. A. WATSON WATT.

5. "The Electric Field of a Thunderstorm and Some of its Effects." By Mr. C. T. R. WILSON, F.R.S.

*6. "The Evidence of Terrestrial Magnetism for the Existence of Highly Ionized Regions in the Upper Atmosphere." By Prof. SYDNEY CHAPMAN, F.R.S.

Proceedings at the Meeting held on November 14, 1924, at the Imperial College of Science.

F. E. SMITH, C.B.E., F.R.S., in the Chair.

1. A Demonstration illustrating "An Electrical Method of Producing Vowel Sounds and its Application to Wireless Telegraphy" was given by Dr. W. H. ECCLES, F.R.S., and C. F. A. WAGSTAFFE.

The apparatus shown represents wireless sending and receiving stations. It was devised to test a proposed method of communication in which the electric waves transmitted could produce easily recognisable chords at a suitably equipped receiving station. It was thought that chords would be more easily recognised than simple tones, and that vowel sounds would be the most easily recognised of chords.

The ideal aimed at in this method of communication is that an operator at one side of the ocean should converse with an operator at the other side by means of a language made up of vowel sounds (somewhat like the Hawaian language), the sounds being produced by pressing keys. Any ordinary language could be converted immediately into this telegraphic language by a code wherein each consonant was represented by a definite pair of vowel sounds. Currents of acoustic frequency need not appear at any stage earlier than in the telephones of the receiving operator. Broadly, the method is as follows:—At the transmitting station the pressing of a key produces immediate electrical oscillations of frequencies 100,800 and 101,300, and waves of these two frequencies are radiated. At the receiving station the waves produce corresponding oscillations, and these are combined with a locally generated frequency of 100,000 cycles per second in the well-known "heterodyne" manner, so as to produce currents of frequencies 800 and 1,300. In order that these should together simulate the vowel sound *ah*, a current of voice frequency, say, 250 cycles per second, should be superimposed in a suitable way; this may be done either before the oscillations leave the sending station or after they reach the receiving station. Each method has given good results with a variety of vowels, made up by taking Paget's table of vowel constituents.

DISCUSSION.

SIR RICHARD PAGET said that the Demonstration proved conclusively that effects of the kind described can actually be obtained. He would suggest experimenting with the simplest form of electrical sound-producers on the lines followed by Mr. J. Q. Stewart, of the Western Electric Company of America, in the testing of telephone receivers. In such apparatus low-frequency resonant circuits are employed and the necessity for heterodyning is avoided; and if, as the speaker believed, consonant sounds consist of not more than four components, it should not be difficult to synthesise ordinary speech in a telephone. Such apparatus would not, of course, be applicable directly to telegraphy, but would be of considerable theoretical interest.

2. A Paper on "The Dielectric Properties of Mica" was read by D. W. DYE, B.Sc., and L. HARTSHORN, A.R.C.S., B.Sc., D.I.C.

Two methods used for determining the dielectric constant of thin sheets of mica are described and the errors discussed.

The results of measurements on over 170 sheets of mica are given. The samples tested included the best clear mica, ruby, green and brown in colour, stained and spotted samples, and also samples with gaseous inclusions. There were also samples of amber mica and silver amber mica.

The results show that practically all samples of muscovite (potassium mica) have the same dielectric constant, the most probable value being 7.0. The presence of inclusions has no great effect on this value. The samples of phlogopite (magnesium mica)—i.e., the amber micas—have rather lower dielectric constants, about 6.0 for normal

amber mica, and 5.0 for the silver amber variety.

Values of power factor are given for many of the samples. For the clear micas (muscovite) it may be as low as 0.003, and possibly less. The effect of inclusions is to increase it considerably. The power factor of the amber micas is greater than that of the muscovite variety—about 0.02 for the clear amber and 0.05 for the silver amber variety.

The samples were all about 8cm. square and 0.1 mm. thick, and the measurements were all made on the Carey Foster bridge at a frequency of 800 cycles per second.

An interesting discussion followed.

3. A Paper on "The X-ray Emission of Electrons from Metal Films, with special Reference to the Region of the Absorption Limit," was read by LEWIS SIMONS, D.Sc., F.Inst.P., Reader in Physics in the University of London.

From both theoretical and experimental viewpoints, it is established that the kinetic energy of emission of electrons from a substance exposed to X-rays may be

$(\frac{1}{2}mv^2)_{K, L, M, \text{ etc.}} = hv - hv_{K, L, M, \text{ etc.}}$

where hv is the energy of the incident quantum and hv_K, L, M, etc., is the energy associated with one of the "quantum absorption limits" of the substance. As the K quantum limit has greater energy than the L.M., etc., limits, it follows that the $K\beta$-rays should have smallest energy. Hence arises the difficulty in giving a quantitative explanation of the selective increase in ionization by collision and absorption when v exceeds v_K.

The problem has been approached experimentally by Barkla and Miss Dallas, who have shown how the total energy of the β-rays from silver (as measured by the ionization produced in H_2) varies with wavelength as the region of the K absorption limit is crossed. The author has now determined directly the aggregate number of β-rays of all types emitted over the same range, and shows thereby, using his own previous observations, and also those of the authors quoted, that no selective change in the average energy occurs when the K flourescent spectrum is excited. It is suggested that this is brought about by a regrouping amongst the numbers and energies of the β-rays constituents, together with the addition of the K group of minimum individual energy as is required by the above equation.

The experimental work has necessitated the separation of the β-rays from the secondary effects they produce, the chief of which is the production of δ-rays of very low energy. The method of this separation is dealt with and the origin of the δ-rays discussed from the points of view of (a) thermionics, (b) recoil electrons, recently brought into prominence by Compton and C. T. R. Wilson, (c) impact electrons. They are impact electrons whose most frequent energy is little greater than 3.5 volts, which seems to be independent of the wavelength producing them, and of the substance from which they come. There are indications that they are influenced at the moment of their departure from the surface, by the scattered X-rays.

A brief discussion followed.

NOTICES OF BOOKS.

THE QUANTUM THEORY: Being Vol. III. of A System of Physical Chemistry, by WILLIAM C. McC. LEWIS, M.A., etc. with diagrams and certain appendices by James Rice, M.A., A. M'Keown, M.Sc., and R. O. Griffith, M.Sc.; VIII. +408 pp.; price, 15/- net: Longmans, Green & Company, Paternoster Row, London.

The importance of this valuable hook is certainly enhanced by the fact that it has been edited by such well-known scientists as Sir William Ramsay, K.C.B., etc., and F. G. Donnan, C.B.E., etc., and its popularity is indicated by the fact that the present is the third edition, which is practical evidence of the appreciation. The work is divided into nine chapters and a number of appendices.

Chapter I is devoted to definitions, and the author defines Probability thus:—

In a purely algebraic sense Probability may be defined as follows: If an event can occur in a ways and fail in b ways, each of these ways being equally likely, then the chance of it occurring is $a/(a+b)$, and the chance or probability of its failing to occur is $b/(a+b)$. The sum of these two terms is necessarily unity, for the sum of the two probabilities covers all eventualities, i.e., the event must either happen or fail, and the

sum represents certainty. It follows that mathematical probability is a fractional *quantity which may be small or large, but* can never exceed unity, i.e., certainty. We may illustrate the ideas by one or two examples. Suppose we have equal numbers of black and white balls inside a bag, the bag being well shaken so as to destroy any possible regularity or ordered arrangement of the balls, what is the probability or chance that, say, a white ball will be drawn from the bag? It is evident that the chance of drawing a white is the same as that of drawing a black. In other words, the probability is one half, for here a=b when a is the number of white and b is the number of black balls and $a/(a+b)=0.5=b/(a+b)$. It is evident that in the limit, if b becomes very small compared with a, the probability *of drawing a white increases almost to* certainty, i.e., the fraction $a/(a+b)$ is nearly unity. We are here considering the probability of a single event occurring. Let us now consider the probability that two independent events may occur *simultaneously*. The probability in such a case is easily *shown* [2] *to be the product of the probabilities* of the separate events. That is, if the probability of the first event is P_1, and that of the second is P_2, then the probability P of both events occurring simultaneously is $P=P_1 P_2$. Thus, if we have two bags, each containing a white balls and b black balls, *the chance of drawing a single white from* the bag is $P_1=a/(a+b)$, and the chance of drawing, say, a black ball from the other bag is P_2, where $P_2=b/(a+b)$. *The chance* of drawing a white ball from the first bag and simultaneously a black ball from the second bag is P where $P=ab/(a+b)^2$. This *simple relation* between the probability of two separate events and the probability that both will occur simultaneously is of great importance, and will be made use of later. Let us now consider one or two cases which possess a more distinctly chemical character.

The first which we shall take is the elementary deduction of the law of mass action given in Vol. I, Chapter III. Suppose we have a gaseous system containing n_a molecules of the substance A, and n_b molecules of the substance B. The probability of a collision between a single molecule of A and a single molecule of B is the product of the *fractional concentration of each, for a* collision is analogous to two events happening simultaneously, which we have just seen depends upon the product of two single *chances, each of which is represented by the* fractional concentration of A and B respectively. We might regard the problem in the following way: Suppose that V is the molecular volume, i.e., the actual volume "occupied" by or allotted to any single molecule of A or B in the mixture. Let V be the *total volume; then* $V=(n_a+n_b)v$. Suppose, for the moment that there is only one molecule of A present. Then the chance that this molecule would occupy a given volume v at a given instant of time would be the ratio of this volume to the total volume, i.e., the ratio v/V or $1/(n_a+n_b)$ If a molecule of A *and a molecule of* B occupy the same position together, this is equivalent to a collision, and hence the chance of a collision is the product of the fractional concentrations. If the reaction required, say, two molecules of A to meet one molecule of B simultaneously the chance of this occurring is

$$\left(\frac{n_a}{n_a+n_b}\right)^2 \frac{n_b}{n_a+n_b}$$ which finally takes

the form: Rate of collision = $kC_a^2.C_b$, for the total volume is proportional to the total *number of molecules present.*

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29247.—Farbenfabriken vorm F. Bayer & Co.—Manufacture of sulphuric acid. Dec. 5th.

28993.—Du Faur, J. B.—Recovery of hydrated oxides of iron and calcium sulphate from sulphate solutions, etc. Dec. 3rd.

28887.—General Chemical Co.—Manufacture of contact sulphuric acid. Dec. 2nd.

28990.—Ikeda, K.—Manufacture of glutamic acid and salts thereof. Dec. 3rd.

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202,311.—Ricard, Allenet, Et Cie.—Process of conversion of gaseous aliphatic ethylene hydrocarbons into liquid hydracarbons.

214,951.—Soc. Chimique Des Usines Du Rhône.—Process for the manufacture of calcium arsenate.

216,129.—Schmidt, Dr. E., and Ges.—Für Chemische Produktion.—Process for obtaining hydrochloric acid free from arsenic.

214,628.—Cassella & Co., Ges. J.—Manufacture of an arsenic compound of the aromatic series.

206,152.—Etablissements Poulenc Freres and Oechslin, C.—Manufacture of hydroxylated aliphatic arsenic acids.

Abstract Published This Week.

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